

The Photochemical Reaction between Nitric Oxide and Isopropanol, Sensitized by Benzophenone

HANS L. J. BÄCKSTRÖM and ALVAR STENERYR

Institutionen för fysikalisk kemi, Chalmers Tekniska Högskola, Göteborg, Sweden

PETER PERLMANN*

Institutet för oorganisk och fysikalisk kemi, Stockholms Högskola, Stockholm, Sweden

The photochemical reaction between isopropanol and nitric oxide with benzophenone as sensitizer has been studied at 25°C using light of wavelength 366 m μ . The results indicate that, in the main reaction, one molecule of acetone, one of nitrogen, one of nitrous oxide, and two of isopropyl nitrite are formed for every six molecules of nitric oxide reacting. A slight side-reaction seems to be connected with the formation of a light-absorbing by-product.

The number of molecules of nitric oxide reacting per light quantum absorbed is given approximately by: $\varphi = \frac{3.5}{1+252c}$, where c is the concentration of NO in mole/l. The retardation of the reaction by nitric oxide must be connected with the fact that a metastable biradical state of benzophenone has to be assumed as an intermediate in the reaction. This biradical state may be identified with the triplet state responsible for the phosphorescence shown by carbonyl compounds in solid solution at low temperatures. Apparently, molecules in this state may be deactivated on collision with nitric oxide molecules before they have time to react with the alcohol. A similar deactivating effect of oxygen has been reported previously.

The mechanism of deactivation is discussed. It is concluded that nitric oxide and oxygen owe their specific deactivating power to their unpaired electrons. In a collision with the biradical, the presence of unpaired electrons in both collision partners must give rise to strong exchange forces that may lead to the formation of a bond. The complex formed, on losing its excitation energy, must be assumed to dissociate again, regenerating the original molecules in their ground states. It is pointed out that the assumed mechanism is in accord with the Wigner spin conservation rule for collisions.

A large number of photochemical reactions of carbonyl compounds are known that can best be interpreted^{1, 2} by assuming that the molecule on light absorption is transformed into a biradical: $R'R''C=O \rightarrow R'R''\dot{C}-\dot{O}$.

* Preliminary experiments, carried out in 1946—47. Present address: Wenner-Grens Institut, Stockholm, Sweden.

Due to the odd electron on oxygen, this biradical will react with many substances by hydrogen abstraction, the free radicals thus formed subsequently undergoing dimerization or disproportionation. Thus, a solution of benzophenone in isopropanol, when irradiated in the absence of oxygen, gives acetone and benzopinacol, $(C_6H_5)_2C(OH)C(OH)(C_6H_5)_2$. In the presence of oxygen, on the other hand, the reaction takes a different course, the free radicals instead reacting with oxygen, with regeneration of benzophenone and formation of acetone and hydrogen peroxide, the net result being a photosensitized oxidation of the alcohol.

As found by Berthoud³, the rate of this photosensitized oxidation decreases with increasing oxygen pressure. This can be explained⁴ by assuming that excited benzophenone molecules in the biradical state may be deactivated on collision with oxygen molecules before they have time to react with the alcohol. Since this specific deactivating power of oxygen might be connected with its paramagnetism it seemed of interest to investigate whether a similar deactivating action is exercised by another paramagnetic gas, nitric oxide.

EXPERIMENTAL

Preliminary work

In the preliminary experiments, essentially the same experimental technique was used as in the earlier work⁴ on the benzophenone-sensitized reaction between alcohols and oxygen. Solutions of benzophenone in 95 % ethanol were shaken with nitric oxide at atmospheric pressure, using a glass shaking tube connected to a gas burette by means of rubber tubing. Irradiation with a mercury arc caused rapid absorption of NO, the main reaction products identified being N_2 , N_2O , and acetaldehyde. Some acetic acid was also formed. The solutions soon turned slightly yellow owing to the formation of small quantities of a coloured by-product which could only be isolated as a brown tar giving a positive test for nitrogen.

The technique employed was not suitable for quantitative determinations. Owing to the formation of gaseous reaction products, one of them highly soluble in the alcohol, there was no simple relation between the measured rate of volume decrease and the rate of nitric oxide absorption. The results of experiments where the nitric oxide was diluted with nitrogen indicated, however, that the rate of reaction increased with decreasing partial pressure of NO. A corresponding effect was to be expected in runs with pure NO, as the partial pressure of NO decreased during the run owing to the accumulation of gaseous reaction products. Such an effect was, indeed, observed, but it was rather weak. Apparently it was masked by a decrease in the rate caused by the formation of the above-mentioned coloured by-product, which acted as an internal light filter. In accordance with this, successively lower rate values were obtained when the same solution was shaken repeatedly with fresh portions of pure NO. In one such experiment, where the total amount of NO absorbed by 15 ml of ethanol + 2.75 mmole of benzophenone was estimated at approximately 80 mmole, 97 % of the benzophenone could be recovered as 2,4-dinitrophenylhydrazone. Thus, benzophenone was not consumed in the reaction but acted merely as a sensitizer.

As in the corresponding reaction with oxygen⁴, isopropanol gave about the same rate as ethanol whereas with methanol the rate was definitely lower (<50 %).

When pure liquid benzophenone was shaken with NO at 60°C in the light of the mercury arc for 2 h, no perceptible reaction took place.

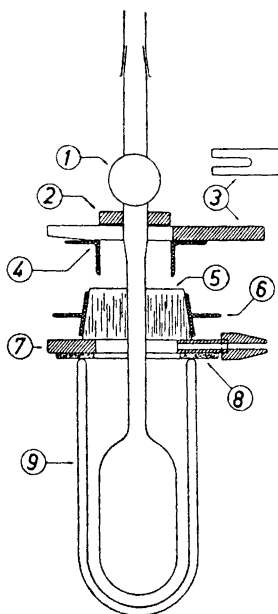


Fig. 1. Shaking tube connected to Töpler system, with arrangements for cooling with liquid oxygen under reduced pressure. (1) Stop-cock. (2) Plexiglas plate, glued on to neck of shaking tube. (3) Plexiglas wedge with groove for neck. (4) Angle-bars attached to vacuum rack. (5) Split rubber stopper with hole fitting neck, held in position by (6) metal ring. (7) Plexiglas ring with evacuation channel. (8) Rubber ring. (9) Dewar vessel with liquid oxygen. When evacuation began, the Dewar with rings 8 and 6 was forced by hand against the rubber stopper, but was soon held in position by the external pressure.

Present work

The alcohol selected for the final experiments was *isopropanol*. In principle, the experimental method employed consisted in allowing the reaction to take place in a closed shaking tube of sufficient size so that a measureable change in composition caused only a moderate decrease in the partial pressure of NO. Remaining nitric oxide as well as the quantities of N_2 and N_2O formed in the reaction were determined by isolating the different gases in the pure state by fractionation at suitable low temperatures and measuring their volumes under standard conditions.

The shaking tube, shown in Fig. 1, was made of thick-walled Pyrex tubing and carried a ground glass joint by means of which it could be attached to the vacuum system, and a stop-cock of such dimensions (bore 11 mm) as to permit the solution to be introduced into the tube by means of a pipette without danger of contamination by stop-cock grease. The wider part of the tube had a diameter of 50 mm and a length of 75 mm, the length of the neck below the stop-cock being 210 mm. The volume was 144.4 ml.

The vacuum system was of conventional type⁵. The arrangements for measuring gas volumes were:

1. A condensation trap connected to a Töpler pump and a calibrated gas burette. This "Töpler system" was connected with the main vacuum line by way of a stop-cock.

2. Another trap connected with a mercury manometer of calibrated bore. This trap-manometer system, also connected to the main line by way of a stop-cock, was used in certain cases for determining larger quantities of condensable gases. It was calibrated

against the gas burette by moving a condensable gas from one system to the other. Its volume at zero pressure was 58.4 ml.

The whole vacuum system was mounted on a rigid stand, made of angle iron. It was evacuated by a two-stage mercury diffusion pump and a fore pump. Vacuum was measured with a Pirani gauge or a McLeod gauge. All stop-cocks were lubricated with Apiezon N*. Removal of NO from the system for discarding was accomplished by adsorption on silica gel at liquid oxygen temperature in a removable trap. This arrangement was also found useful for over-night pumping-off of adsorbed gases from the system. A side-tube with a stop-cock and a ground glass joint enabled the shaking tube to be attached to the Töpler system.

The vapour pressure of nitric oxide at the temperature of liquid oxygen (90°K) is 3.3 mm. For a satisfactory separation of this gas from nitrogen it was therefore necessary to reach lower temperatures by cooling with liquid oxygen under reduced pressure. Arrangements for accomplishing this without strain on the glass parts are shown in Fig. 1. A similar arrangement was used for cooling the manometer trap. A copper gauze immersed in the liquid oxygen served to increase thermal conduction. Using pumps of sufficient capacity, temperatures of 63–65°K, as indicated by the equilibrium oxygen pressure, were reached without difficulty, corresponding to a nitric oxide pressure of about 5×10^{-4} mm.

The shaking experiments were performed at 25°C in a thermostat with a quartz window. The light source was a vertical 220 V AC mercury arc (LK 700) from Lumalamp, Stockholm, burned in series with a regulating resistance. Voltage variations were eliminated by means of a Sorensen constant voltage regulator. Relative values of the radiation intensity at 366 $m\mu$ (the only mercury line transmitted by the wall of the shaking tube and absorbed by the solution) were obtained with the aid of a thermopile and galvanometer as described earlier⁴.

Materials

Nitric oxide was prepared in a special vacuum system from potassium nitrite, potassium iodide and sulfuric acid by the method of Winkler. It was freed from iodine vapour and higher oxides by passage through two large wash bottles with 50 % potassium hydroxide solution in which it was finely dispersed by means of fritted glass disks, and dried by passing through a trap at -79°C . It was then condensed at 90°K and freed from N_2O and N_2 by fractionation according to Gray⁶. The purified gas was collected in an evacuated glass bulb with stop-cock, which was later sealed to the main vacuum system.

Nitrogen was prepared by heating sodium azide in an evacuated glass system as described by Justi⁷. It was stored in the same way as NO.

Nitrous oxide. The commercial product was introduced into the vacuum system and dried by passing through a trap at -79°C . Volatile impurities were removed by pumping at 90°K.

Isopropanol. C.P. isopropanol was fractionally distilled at atmospheric pressure. Only the middle fractions were used.

Benzophenone. Merck's benzophenone, "M.P. ca. 48°C ", previously found to be of satisfactory purity⁴, was freed from traces of volatile impurities by melting in a vacuum.

Experimental procedure

In starting an experiment, 2 g of benzophenone were dissolved in 26 ml of isopropanol, and 25 ml of the solution introduced into the shaking tube. The tube was then attached to the Töpler system and cooled to 90°K and the air removed by pumping. With the stop-cock closed, the tube was then allowed to warm to room temperature, again cooled to 90°K, the pumping repeated, and so on, until pressure readings indicated that dissolved gases had been completely removed. Generally three such pumpings sufficed. An accurately measured quantity of NO was then condensed in the tube, whereupon the stop-cock was closed and the tube disconnected from the vacuum system.

* Much time was wasted in trying to use commercial silicone grease. No satisfactory vacuum could be maintained with this lubricant.

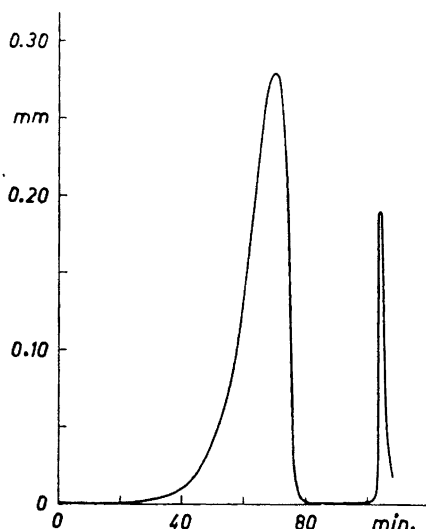


Fig. 2. Change of pressure with time during low-temperature distillation of a nitrous oxide-isopropanol mixture.

After an experiment, the shaking tube was again attached to the Töpler system and cooled to 64°K whereupon uncondensed gas (nitrogen) was pumped into the gas burette by means of the Töpler pump. This was repeated twice, with intermediate thawing of the solution, after which the nitrogen was recirculated through the Töpler trap, kept at -79°C , to remove alcohol vapour, and its volume again measured.

With the shaking tube at 90°K, unreacted NO was then sublimed into the manometer trap, kept at 64°K. This was repeated several times with intermediate thawing of the solution. The gas was freed from alcohol vapour by recirculation and its volume determined.

The determination of N_2O presented difficulties because of its high boiling point (-89°C) and its high solubility in the alcohol. The method finally arrived at was as follows.

With the shaking tube at about -25°C , the Dewar vessel was removed and a brass container in two parts, lined with asbestos, was placed around the neck of the tube and filled with pulverized CO_2 -ice. The length of the cooled part of the tube was about 8 cm. The tube was then opened to the evacuated Töpler system (volume about 425 ml). The heating action of the surrounding air caused the solution to boil with reflux under a pressure which increased as nitrous oxide collected in the Töpler system. Approximate values of the pressure were obtained by observing the mercury levels in the two limbs of the gas burette. When after some hours no further increase in pressure was observed, the stop-cock of the shaking tube was closed, the Töpler system opened to the main line, and the gas obtained condensed in the manometer trap with liquid oxygen. The process was repeated twice, using a smaller volume (about 70 ml) to receive the gas, the shaking tube being connected only to the gas burette.

Attempts to separate the nitrous oxide from admixed alcohol vapour by recirculation through a trap at -79°C were unsuccessful. A satisfactory separation was, however, obtained in the following manner.

The bottom of the Töpler trap was covered with mercury (weight about 20 g). The gas was carefully condensed in the lowest part of this trap by cooling only the bottom with liquid oxygen. The whole trap was then brought to liquid oxygen temperature, the Dewar vessel rapidly replaced by an empty Dewar precooled to the same temperature, and the neck covered with cotton wool. The Töpler system was opened to the manometer trap, which was immersed in liquid oxygen, and the pressure read at regular intervals on the Pirani gauge.

The result of one of the model experiments, using a mixture of 216 μ mole N_2O and 8 μ mole isopropanol vapour, is shown graphically in Fig. 2. After the first pressure maximum, caused by distillation of N_2O , the pressure soon dropped to 1 or 2×10^{-3} mm. When this pressure had been maintained for 19 min, the Dewar vessel was, in this case, removed (at "100 min") in order to speed up the process. The second maximum, caused by distillation of the alcohol, appeared shortly after the mercury had melted.

The good separation obtained is ascribed to the heat capacity and thermal conductivity of the mercury lump, slowing down the heating process and causing evaporation to take place from a surface of more uniform temperature. When the method was used for the determination of N_2O , the stop-cock of the manometer trap was closed as soon as the pressure, after passing the first maximum, had reached a level of 1 or 2×10^{-3} mm. The Dewar vessel was removed, the trap allowed to reach room temperature, and the quantity of N_2O determined by reading the manometer.

The whole procedure for determining N_2O was tested by condensing measured quantities in the shaking tube. Before starting the analysis, the gas was allowed time to dissolve in the alcohol at room temperature. The following results were obtained. Throughout this paper, gas volumes are given in ml at 20°C and 760 mm.

Quantity of N_2O used, ml	5.44	9.71
" " " found, ml	5.43	9.71

After completing the analyses for the above-mentioned reaction products, any volatile constituents that might have escaped into the vacuum system and become adsorbed on the walls were again collected in the shaking tube by cooling the latter with liquid oxygen for a sufficient length of time. The solutions were then analyzed for acetone as described earlier⁴, except that a photoelectric spectrophotometer, Beckman Model DU, was used. They were then stored in glass-stoppered bottles in the dark for further examination on a later occasion.

RESULTS

As shown by Table 1, nitrogen and nitrous oxide are formed in equimolar quantities irrespective of experimental conditions. Further details in connection with the experiments are given in Table 2.

Table 1. The relation between the quantities of nitrogen and nitrous oxide formed in the reaction.

Experiment No.	5	6	7	9	10
N ₂ formed, ml	3.73	0.74	2.71	4.94	7.54
N ₂ O " "	3.73	0.73	2.70	5.13	7.36

In Table 2, the experiments are arranged in chronological order. In the first five experiments (series I), that were of an orientating nature, the current through the lamp was kept constant at 5.00 A but no intensity measurements were made. The rate of reaction was inconveniently high. The rest of the experiments were therefore made at lower intensities, corresponding to galvanometer deflections of about 2.6 cm in experiments 6—12 (series II), and 6.0 cm in experiments 13—20 (series III). Column 3 gives the average galvanometer deflection during the run in cm.

Table 3 summarizes derived values for runs in presence of nitric oxide. Column 2 gives the average quantity of NO present in ml, columns 3 and 4 moles of nitrogen and acetone formed per mole of NO consumed, and column 5 the rate of reaction expressed as μ moles of NO consumed per minute. The

Table 2. Results of systematic experiments as regards nitric oxide consumed and nitrogen and acetone formed under different experimental conditions.

1 Expt. No.	2 Time, min	3 Light intensity	4 NO added, ml	5 NO con- sumed, ml	6 Nitrogen, ml	7 Acetone, μ mole
1	15	—	—	—	—	1 050
2	7	—	112.3	26.3	3.59	169
3	3	—	36.90	22.15	5.36	146
4	1	—	18.25	8.76	1.20	73
5	5	—	74.63	27.69	3.73	169
6	3	2.62	20.84	4.55	0.74	31
7	32	2.59	111.00	19.71	2.71	110
8	25	2.56	80.10	20.16	2.70	119
9	45	2.61	79.88	37.08	4.94	239
10	65	2.62	80.11	52.42	7.54	350
11	30	2.62	—	—	—	396
12	30	2.62	—	—	—	398
13	9	6.00	—	—	—	293
14	9.5	6.00	—	—	—	295
15	1.5	6.00	19.62	5.40	0.82	34
16	15	6.00	115.86	20.65	2.94	131
17	10	6.00	94.53	17.05	2.36	102
18	6	6.00	67.66	12.29	1.75	76
19	3	6.00	42.92	7.58	1.15	52
20	10	6.00	96.78	15.57	2.35	—

strongly deviating values within brackets may probably be ascribed to experimental errors and are left out of consideration. In Fig. 3, the remaining values in columns 3 and 4 are plotted against consumed NO in ml. The points show considerable scattering but nevertheless an unmistakable trend, especially as regards the nitrogen values. The conclusion seems justified that the main

Table 3. 1) Nitrogen and acetone formed in the reaction in relation to nitric oxide consumed (mole/mole); 2) rate of nitric oxide absorption in μ mole min^{-1} .

1 Expt. No.	2 NO ml	3 $\frac{\text{N}_2}{\text{NO}}$	4 $\frac{\text{Acetone}}{\text{NO}}$	5 NO consumed μ mole/min
2	99.1	0.137	0.155	156
3	25.8	(0.242)	0.159	307
4	13.9	0.137	(0.200)	364
5	60.8	0.135	0.147	230
6	18.6	0.163	0.164	63.1
7	101.0	0.138	0.134	25.6
8	70.0	0.134	0.142	33.5
9	61.3	0.133	0.155	34.3
10	53.9	0.144	0.161	33.5
15	16.9	0.152	0.151	149.7
16	105.5	0.142	0.153	57.2
17	86.0	0.138	0.144	70.9
18	61.5	0.142	0.149	85.2
19	39.1	0.152	0.165	105.1
20	89.0	0.151	—	64.7

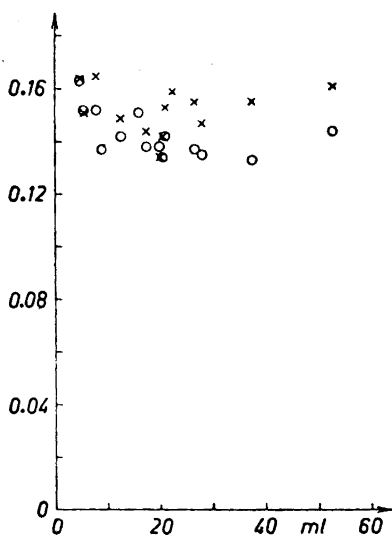


Fig. 3. Yields of nitrogen (O) and acetone (x) (mole per mole of NO) as a function of total NO absorbed (ml).

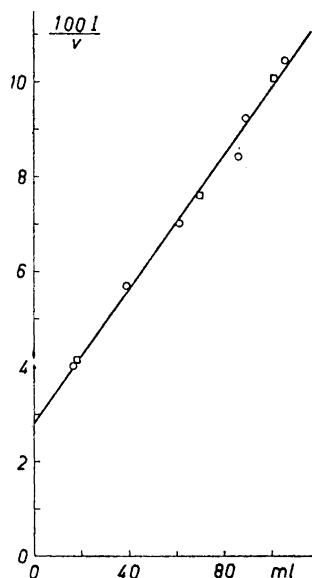


Fig. 4. Plot of $\frac{100 I}{v}$ against initial nitric oxide in ml. I = average galvanometer deflection during run in cm, v = rate of nitric oxide absorption in $\mu\text{mole min}^{-1}$. \square Series II, \circ Series III. The straight line corresponds to the calculated rate equation (see text).

reaction gives rise to one molecule of acetone, one of nitrogen, and one of nitrous oxide, for every 6 molecules of nitric oxide reacting, but that the yields of nitrogen and nitrous oxide are markedly reduced as the reaction proceeds, in connection with a side-reaction. As in the preliminary work on ethanol, the solutions turned slightly yellow. In runs 6–10 the increase in light absorption at $366 \text{ m}\mu$ was followed spectrophotometrically by diluting 1-ml samples with 2 ml of isopropanol, and measuring the extinction in a layer-thickness of 1 mm. The values found were 0.667, 0.680, 0.680, 0.695, 0.722, as against 0.645 in a blank determination, thus increasing regularly with the amount of NO absorbed (see Table 2).

As shown by Table 3, the rate of nitric oxide absorption at constant light intensity generally decreases with increasing NO concentration, as measured by the average quantity of NO present during the run. However, runs 8, 9, and 10, show that the decrease in NO concentration taking place as a result of the reaction does not lead to a corresponding increase in reaction rate. In runs 9 and 10, the amount of NO initially present was the same as in run 8, but the percentage conversion was considerably increased by increasing the time of irradiation. The results indicate that the increase in rate normally

associated with decreasing NO concentration is here very nearly compensated by a decrease caused by the change in light absorption, an increasing fraction of the active light being absorbed by the coloured by-product formed. Under these circumstances it seems correct to relate the observed reaction rate to the quantity of NO initially present rather than to the average during the run. This has been done in Fig. 4.

In calculating the best straight line through the points by the method of least squares, runs 9 and 10 were excluded. The equation found was $\frac{100 I}{v} = 2.73(1 + 0.0239[\text{NO}])$.

The observed rates of acetone formation in the runs without nitric oxide, recalculated to a galvanometer deflection of 1 cm and expressed in $\mu\text{mole}/\text{min}$, were as follows:

Run No.	11	12	13	14	Average
Rate of acetone formation	5.04	5.07	5.43	5.18	5.18

Assuming a quantum efficiency of 0.5 (see page 18), the number of quanta absorbed by the solution per minute becomes $1.04 \times I \times N \times 10^{-5}$, where I represents the galvanometer deflection in cm, and N Avogadro's number. On this basis, the following formula is obtained for the quantum efficiency of nitric oxide absorption:

$$\varphi_{\text{NO}} = \frac{3.5}{1 + 0.0239[\text{NO}]} \quad *$$

Nitrite determinations

The quantities of nitrogen and nitrous oxide formed in the reaction will account for at most 2/3 of the nitric oxide consumed. A search was therefore made for other nitrogenous reaction products. A qualitative test revealed the presence of nitrite. Attempts were accordingly made to obtain a method for determining nitrites in the reaction mixture, based on the usual spectrophotometric method for nitrite determination in water.

In the procedure of Rider and Mellon ⁸, nitrite is made to react with sulfanilic acid in strongly acidic solution and the resulting diazonium salt coupled with α -naphthylamine after buffering with sodium acetate in order to speed up the coupling reaction. As alkyl nitrites are very rapidly hydrolyzed in acid solution ⁹, this method can also be used for determining alkyl nitrites. In view of the presence of benzophenone in the reaction mixtures, we tried to work in alcoholic solutions. Experiments with pure sodium nitrite showed that the coupling process, when performed in 50 % ethanol, was completed in less than 10 min at room temperature even without buffering the solution. The addition of sodium acetate was therefore omitted. The presence of the alcohol greatly increased the stability of the resulting dyestuff solution, the extinction remaining unchanged for more than 3 h. Whether the diazotization was carried out in water or in 95 % ethanol was without influence on the final result. A diazotization time of 10 min was sufficient.

* A possible source of error in the runs without nitric oxide, which was not realized at the time, is the different behaviour of the solution when shaken with or without added gas. It would have been better to add an inert gas like nitrogen. As it is, light absorption may have been less complete than in the other runs which would lower the rate of acetone formation and cause the calculated values of φ_{NO} to come out too high.

The molar decadic extinction coefficient of the dyestuff at 520 $m\mu$ was found to be 4.30×10^4 l mole⁻¹cm⁻¹.

In studying the application of the method to alkyl nitrites, model experiments were made with redistilled amyl nitrite of 88.9 % purity, as determined by the method of van Itallie, Steenhauer and Harmsma¹⁰. No entirely satisfactory method was obtained. Results in the presence of benzophenone tended to be low and were not very reproducible. In the method finally adopted, the nitrite was therefore separated from the benzophenone by distillation. A sample of the reaction mixture was suitably diluted with ethanol. 1 ml of the resulting solution was rapidly introduced into a distillation apparatus of special design where it was subsequently mixed with 5 ml of 25 % ethanol and the nitrite distilled off as ethyl nitrite¹¹ in a current of oxygen at 70–75°C. The vapours were absorbed in 25 ml of ice-cold 95 % ethanol mixed with 1 ml of sulfanilic acid solution (0.6 g of sulfanilic acid + 20 ml of concentrated hydrochloric acid + water to 100 ml). The distillation was continued for 20 min, after which the alcoholic sulfanilic acid solution was transferred to a measuring flask, mixed with 1 ml of naphthylamine reagent (0.6 g of α -naphthylamine + 1 ml of concentrated hydrochloric acid + water to 100 ml) and diluted with water to 50 ml. After standing at least 10 min, the extinction was measured at 520 $m\mu$, using a layer-thickness of 1 cm.

In model experiments, the results obtained by this method were fairly reproducible but they were consistently about 10 % low (90.5 ± 1 % of the theoretical value). In Table 4, the experimental values have therefore been multiplied by a factor of 1.1. They are given in moles of nitrite per mole of nitric oxide absorbed.

Table 4. Quantities of nitrite found in relation to nitric oxide consumed in the reaction (mole/mole).

Expt. No.	6	7	8	9	10	15	16	17	18	19	20
$\frac{\text{Nitrite}}{\text{NO}}$	0.116	0.088	0.097	0.262	0.239	0.131	0.293	0.234	0.306	0.168	0.273

Isopropyl nitrite is highly volatile (B.P. 45°C) and losses by evaporation may therefore have taken place during the long time of storing the reaction mixtures (from 2 to more than 6 months). This was definitely the case with the solution from experiment No. 15, for which determinations made 2 months previously by a preliminary method, without distillation, had given values of 0.264 and 0.266. Taken as a whole, the evidence seems to support the assumption that, in the main reaction, one third of the nitric oxide reacts to form *iso*-propyl nitrite.

Solubility of nitric oxide in *isopropanol*

The solubility of nitric oxide in *isopropanol* at 25°C was determined, using an apparatus similar to the shaking tube (Fig. 1), except that it had two bulbs above each other. The lower bulb, containing the alcohol, was furnished with a magnetic stirrer. The stop-cock connecting the bulbs had a bore of 11 mm to facilitate gas diffusion. After greasing the stop-cocks, the apparatus was connected to the vacuum system, and dissolved air was removed as described earlier. Because of the large quantity of *isopropanol* used, 8 successive pumping operations were required. To avoid cracking of the glass tube surrounding the magnetic stirring rod, on solidification of the alcohol, the tube had to be made of thick glass, and with pointed ends. Starting at these points, cracks were formed in the solidified alcohol, thus relieving the strain on the tube.

After condensing a measured volume of NO in the apparatus, it was disconnected from the vacuum system, surrounded by a polythene bag and immersed in a water thermostat at 25.0°C. After 5 h, with the magnetic stirrer operated at such speed that a marked indentation was observed in the alcohol surface, the stop-cock between the bulbs was closed and the apparatus again connected to the vacuum system. The NO in the upper bulb was condensed in the manometer trap at 64°K, freed from alcohol by trap to trap distillation, and measured in the gas burette. All gas volumes were measured at three different pressures to diminish the effect of calibration errors.

The following results were obtained.

Total nitric oxide used, ml	17.46	6.425
Nitric oxide in upper bulb, ml	11.035	4.05

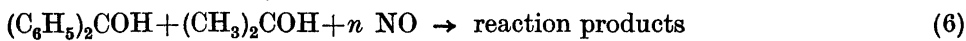
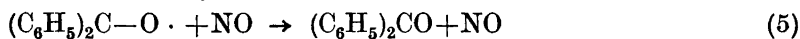
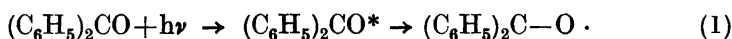
The volumes, as determined by weighing, were: upper bulb, 143.3 ml; both bulbs including the stop-cock but excluding the magnetic stirrer, 333.6 ml; isopropanol, 149.9 ml. The values calculated for the Ostwald solubility coefficient are 0.287 and 0.291, respectively. Mean value 0.289.

In the experimental formula for φ_{NO} (p. 16) the concentration of NO is given as the quantity of NO initially present in the reacting system, expressed in ml at 20°C and 760 mm of mercury. Knowing the volume of the shaking tube (144.4 ml), the volume of the solution (25 ml), and the partition coefficient, (0.289), the corresponding concentration of NO in the solution in mole/l c_{NO} , can be calculated. The formula then becomes

$$\varphi_{\text{NO}} = \frac{3.5}{1 + 252 c_{\text{NO}}}$$

DISCUSSION

The following mechanism, similar to the one proposed for the corresponding reaction with oxygen⁴, will account for the main features of the results obtained.



The reaction in the absence of nitric oxide is determined by steps (1)–(4), giving a quantum efficiency of 0.5 for the formation of benzopinacol and acetone*. In the presence of nitric oxide, the reaction is determined by steps (1), (2), (5), and (6). Assuming stationary state concentration for the intermediate

* Preliminary results obtained by C. Åquist in this laboratory indicate that the true value is between 0.47 and 0.57. The investigation is being continued.

radicals, and on condition that n is constant, the following expression is obtained for the quantum efficiency of nitric oxide absorption:

$$\varphi_{\text{NO}} = \frac{n}{1 + \frac{k_5 c_{\text{NO}}}{k_2 c_A}}$$

where c_A denotes the concentration of isopropanol.

The most important steps in the reaction mechanism will now be discussed separately.

The activation of benzophenone by light absorption

The biradical state of benzophenone appearing in the reaction scheme may be identified with the metastable triplet state responsible for the phosphorescence exhibited by carbonyl compounds in solid solution at liquid air temperatures¹². Absorption of long-wave ultraviolet light raises the molecules to the lowest excited singlet state, from which they pass, by a process of radiationless internal conversion, to a slightly lower lying triplet level, the energy given out in the process being taken up by the surrounding solvent molecules as vibrational energy. In accordance with the selection rule prohibiting inter-combinations between levels of different multiplicity, the radiative return from the triplet to the ground (singlet) level is a slow process. The rate of decay of phosphorescence under the conditions specified gives an approximate measure of the natural mean life-time of the triplet state. The value found for benzophenone¹³ is 0.008 sec.

A change from a singlet to a triplet state means the unpairing of two electrons in the molecule, *i.e.* the formation of a biradical. As the structure of the triplet state of carbonyl compounds Lewis and Kasha¹² suggested a molecule in which one member of the double bond of the carbonyl group had been broken. Apparently, they were not aware of the wealth of photochemical evidence which had caused one of us¹ to postulate the existence of a biradical of this kind as an intermediate in a large group of photochemical reactions of carbonyl compounds.

In fluid solvents at ordinary temperatures the same process of internal conversion to the triplet state may be expected to take place, but the life-time of the biradicals will normally be shortened by deactivating collisions with solvent molecules to such an extent that no phosphorescence is observed under these conditions. This is the case with benzophenone. Apparently, however, the life-time is long enough for photochemical reactions to take place with suitable reaction partners.

Substances showing phosphorescence in solid solution at liquid air temperatures generally also show normal fluorescence, *i.e.* the much more short-lived radiation connected with the return from the excited singlet to the ground state. According to Kasha¹⁴, however, fluorescence is scarcely to be observed in the case of carbonyl compounds, showing that the "forbidden" conversion to the triplet state is essentially complete. He gives the ratio of the yield of fluorescence to that of phosphorescence as $\leq 10^{-3}$. Since the natural life-time of the

excited singlet state is probably of the order of 10^{-8} sec, this means that the time required for its conversion to the triplet state under the conditions of the experiments is of the order of 10^{-11} sec.

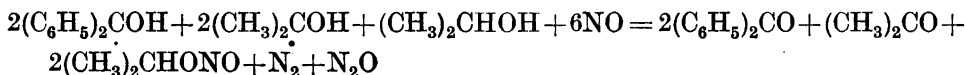
The quantum efficiency of phosphorescence of benzophenone dissolved in EPA glass (a mixture of ether, pentane, and alcohol) at 77°K has been determined by Gilmore, Gibson and McClure¹³, who found a value of $0.84 \pm 10\%$. There is reason to believe, however, that this is less than the natural value since it has been found^{15, 16} that phosphorescent substances react photochemically with the ethanol in the solvent even at these low temperatures.

The assumption underlying step (1) in the reaction mechanism that one biradical is formed for every light quantum absorbed, thus seems to be in accord not only with the photochemical evidence⁴ but also with the results of phosphorescence studies.

The reaction products

The analytical results indicate that, in the main reaction, 1 molecule of nitrogen, 1 of nitrous oxide, 1 of acetone, and 2 of *isopropyl* nitrite are formed for every 6 molecules of nitric oxide taken up by the solution. The experimental formula for φ_{NO} (p. 18), when extrapolated to zero nitric oxide concentration, gives 3.5 molecules of NO reacting for every light quantum absorbed. A value of 3.0 would make the extrapolated quantum yields for the reaction products 0.5 and 1, respectively. We accordingly assume n in step (6) to be = 3.

If step (6) is written for 2 light quanta absorbed and in such a way that it will account for the analytical results of the present investigation as well as for the fact, established in the preliminary experiments, that benzophenone is not consumed in the reaction, it becomes:



This equation is not balanced, 4 hydrogen atoms and 3 oxygen atoms remaining to be accounted for. The formation of one molecule of water seems likely, but the complete elucidation of the stoichiometry will require further work. We have searched the literature in vain for reactions of NO giving N_2 and N_2O in equimolar quantities. For the present we are not prepared to make any suggestions as to the probable course of the reaction. One point should be mentioned, however. The fact that nitrites are formed in the reaction might suggest that the radical formed from the alcohol in step (2) is not $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ but the alkoxy radical $(\text{CH}_3)_2\text{CHO}\cdot$, since alkoxy radicals are known to add on nitric oxide to form nitrites¹⁷. In several cases it has been proved definitely, however, that free radicals react with alcohols by abstracting a hydrogen atom from the α -carbon atom¹⁸. A case which is of particular interest in the present connection is the one reported by Symons and Townsend¹⁶.

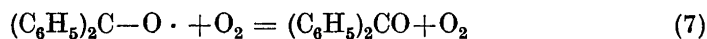
For the purpose of the present investigation, however, the only important question is whether the value of n in step (6) is constant or not. The results indicate that this is true for the main reaction and, as explained earlier (p. 16),

the method of correlating the observed reaction rate with the initial concentration of NO rather than with the average during the run should have largely eliminated the effect of the side reaction on the rate equation.

The formula previously found for the rate of the corresponding reaction with oxygen at 25°C under the experimental conditions used⁴, as a function of the oxygen pressure, when recalculated using the known Ostwald solubility coefficient of oxygen in *isopropanol*¹⁹, 0.2463, becomes

$$v = \frac{43.5}{1 \times 95c_{\text{ox}}}$$

where c_{ox} is the concentration of oxygen in mole/l. The denominator in this expression is $= 1 + \frac{k_7c_{\text{ox}}}{k_2c_A}$, where k_7 is the rate constant for the reaction:



Comparison with the expression for φ_{NO} shows that the rate constants of reactions (5) and (7) are of the same order of magnitude. This was to be expected since both reactions may be presumed to be so rapid as to be essentially diffusion-controlled²⁰. This means that the rate constants in *isopropanol* at 25°C should approach a calculated limiting value²¹ of about 3.5×10^9 l mole⁻¹sec⁻¹. On this basis it is found that the mean life of the biradical in pure *isopropanol* is about 10⁻⁷ sec and that only one collision with *isopropanol* molecules in about 10⁶ leads to reaction²².

The mechanism of deactivation by NO and O₂

The analogy between the deactivation process represented by step (5) of the proposed reaction mechanism and the phenomenon of fluorescence quenching was emphasized in an earlier paper⁴. In recent studies of the fluorescence of organic compounds in the vapour state it has been found that O₂ and NO are, without exception, equally effective as quenchers. The substances studied were, anthraquinone and a number of its derivatives²³, anthracene and two related hydrocarbons²⁴, and β -naphthylamine²⁵. The results are interpreted in terms of a theory advanced by Karyakin, Terenin and Kalenichenko²³. The quenching is assumed to be "paramagnetic", collisions with the paramagnetic quencher molecules enabling an otherwise forbidden transition of the singlet excited fluorescer molecule to a somewhat lower lying triplet level to take place. It is an essential feature of the theory that, for the paramagnetic mechanism to be effective, the energy difference between the excited singlet and the triplet levels should be small. In cases where this difference was of the order of 0.2 eV the efficiency of the quenching collisions was found to be = 1 for both O₂ and NO whereas no quenching was observed by either gas when it amounted to 0.8 eV.

The present case is, however, altogether different from the one discussed above. What we are dealing with is the interaction between a molecule of nitric oxide or oxygen and an excited benzophenone molecule which is not in a singlet but in a triplet state. The energy of the triplet state is 3.0 eV above

the ground (singlet) level¹². Transition to the ground state by a paramagnetic mechanism appears to be a highly improbable event.

There can be little doubt, however, that the unpaired electrons of NO and O₂, that cause their paramagnetism, are also responsible for their deactivating power. In a collision with a benzophenone molecule in the biradical state, the presence of unpaired electrons in both collision partners must give rise to strong exchange forces that may lead to bond formation. The property of NO and O₂ of undergoing addition reactions with free radicals is well known. To explain the experimental results, the reaction product must be assumed only to be stable in the excited state (*cf.* Förster and Kasper²⁶) and to dissociate into the original molecules in their ground states when the excitation energy is lost through collisions with neighbouring molecules*. The assumption of a quenching mechanism of this kind receives support from theoretical considerations of the ways in which electronic energy may be transformed into thermal energy²⁷. It is also in accord with the Wigner spin-conservation rule for collisions²⁸ and thus involves no forbidden transitions. It should therefore have a high intrinsic probability.

Not every collision between the biradical and a molecule of O₂ or NO may be expected to lead to bond formation. For this to happen, the spins must be favourably oriented and presumably also other steric requirements have to be met. In addition, an energy of activation may be involved, although this can hardly be expected to be large²⁹. However, the influence of these factors on the rate of the quenching reaction should be much less in solution than in the gas phase. In solution, the rate of reaction is governed primarily by the rate of diffusion of the reactants toward each other. As shown by Rabinowitch³⁰, the diffusion process leads to an "encounter", a set of collisions. These repeated collisions, in conjunction with molecular rotation, should markedly increase the probability of reaction. It seems significant that the rate of quenching by oxygen of the long-lived fluorescence of biacetyl in the vapour state³¹ corresponds to a steric factor of about 0.1, whereas the rate in benzene solution³² approaches 50 % of the limiting value for a diffusion-controlled reaction.

In view of the above considerations, the most probable explanation of the lower deactivating efficiency of O₂ as compared to NO, which cannot be due to a difference in diffusion rate, would seem to be a difference in activation energy.

Acknowledgement. The authors gratefully acknowledge the support of this work by *Statens Naturvetenskapliga Forskningsråd*.

REFERENCES

1. Bäckström, H. L. J. *Z. physik. Chem.* **B25** (1934) 99.
2. Hirschberg, Y. and Farkas, L. *J. Am. Chem. Soc.* **59** (1937) 2453.
3. Berthoud, A. *Helv. Chim. Acta* **16** (1933) 592.

* In the analogous case of the long-lived fluorescence of biacetyl vapour, which according to Lewis and Kasha (*J. Am. Chem. Soc.* **67** (1945) 1000) is a triplet → singlet transition, quenching by oxygen leads to a permanent oxidation of the fluorescer (Almy, G. M., Fuller, H. Q. and Kinzer, G. D. *Phys. Rev.* **55** (1939) 238).

4. Bäckström, H. L. J. *The Svedberg 1884—1944*, Almquist & Wiksells Boktryckeri, Uppsala, 1944, p. 45.
5. Sanderson, R. T. *Vacuum Manipulation of Volatile Compounds*, John Wiley & Sons, Inc., New York 1948.
6. Gray, R. W. *J. Chem. Soc.* **87** (1905) 1605.
7. Justi, E. *Ann. Physik* [5] **10** (1931) 985.
8. Rider, B. F. and Mellon, M. G. *Ind. Eng. Chem. Anal. Ed.* **18** (1946) 96.
9. Fischer, W. M. *Z. physik. Chem.* **65** (1909) 61.
10. van Itallie, L., Steenhauer, A. J. and Harmsma, A. *Pharm. Weekblad* **66** (1929) 15; *Chem. Zentr.* **1929:1**, 1245.
11. Bertoni, G. *Gazz. chim. ital.* **12** (1882) 438.
12. Lewis, G. N. and Kasha, M. *J. Am. Chem. Soc.* **66** (1944) 2100.
13. Gilmore, E. H., Gibson, G. E. and McClure, D. S. *J. Chem. Phys.* **20** (1952) 829; **23** (1955) 399.
14. Kasha, M. *Discussions Faraday Soc. No. 9* (1950) 14.
15. Gibson, G. E., Blake, N. and Kalm, M. *J. Chem. Phys.* **21** (1953) 1000.
16. Symons, C. R. and Townsend, M. *Ibid.* **25** (1956) 1299.
17. Levy, J. B. *J. Am. Chem. Soc.* **75** (1953) 1801; **76** (1954) 3790.
18. Kharasch, M. S., Rowe, J. L. and Urry, W. H. *J. Org. Chem.* **16** (1951) 905; Urry, W. H., Stacey, F. W., Huyser, E. S. and Juveland, O. O. *J. Am. Chem. Soc.* **76** (1954) 450.
19. Kretschmer, C. B., Nowakowska, J. and Wiebe, R. *Ind. Eng. Chem.* **38** (1946) 506.
20. Förster, Th. *Fluoreszenz organischer Verbindungen*, Vandenhoeck & Ruprecht, Göttingen 1951, p. 209.
21. Debye, P. *Trans. Electrochem. Soc.* **82** (1942) 265.
22. Moelwyn-Hughes, E. A. *Trans. Chem. Soc.* **1932**, 95.
23. Karyakin, A. W., Terenin, A. N. and Kalenichenko, Y. I. *Doklady Akad. Nauk S.S.S.R.* **67** (1949) 305.
24. Stevens, B. *Trans. Faraday Soc.* **51** (1955) 610.
25. Dubois, J. T. *J. Chem. Phys.* **25** (1956) 178.
26. Förster, Th. and Kasper, K. *Z. Elektrochem.* **59** (1955) 976.
27. Franck, J. and Levi, H. *Z. physik. Chem. B* **27** (1934) 409; Franck, J. and Sponer, H. Volume commemoratif Victor Henri: "Contribution à l'Étude de la Structure Moléculaire", 1948, p. 169.
28. Laidler, K. J. *The Chemical Kinetics of Excited States*, Oxford University Press, Oxford 1955, p. 32, 100.
29. Williamson, B. and La Mer, V. K. *J. Am. Chem. Soc.* **70** (1948) 717.
30. Rabinowitch, E. *Trans. Faraday Soc.* **33** (1937) 1225.
31. Coward, N. A. and Noyes, W. A. *J. Chem. Phys.* **22** (1954) 1207.
32. Bäckström, H. L. J. and Sandros, K. *J. Chem. Phys.* **23** (1955) 2197.

Received September 11, 1957.