

## Formation of Charge-transfer Complexes between Free Radicals in the Photoreduction of Benzophenone by Isopropanol

HANS L. J. BÄCKSTRÖM, K. LENNART APPELGREN and  
RUNE J. V. NIKLASSON

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

As shown by Schenck and by Pitts, the photoreduction of benzophenone by isopropanol in the absence of oxygen leads to the formation not only of benzopinacol and acetone, but also of small quantities of a substance characterized by a strong long-wave absorption band ( $\lambda_{\max}$  ca. 325  $m\mu$ ). This substance, which we denote by  $M_I$ , has been supposed to be an intermediate of radical nature.

We have irradiated oxygen-free benzophenone solutions in isopropanol of concentrations  $< 10^{-4}$  M with light of wavelength 253.7  $m\mu$  and of known absolute intensity, and studied the changes in absorbance at this wavelength and at 334  $m\mu$ . The results have shown that at low benzophenone concentrations  $M_I$  is the main reaction product, in the limiting case of extreme dilution the only reaction product; and that only one molecule of benzophenone is consumed in the formation of a molecule of  $M_I$ . The primary products formed in the reaction between a photoactivated benzophenone molecule and a molecule of isopropanol are known to be the radicals  $Me_2\dot{C}OH$  (I) and  $Ph_2\dot{C}OH$  (II). We have reached the conclusion that  $M_I$  must be a charge-transfer complex formed by these two radicals.

With increasing benzophenone concentration the yield of  $M_I$  decreases, which is interpreted as the result of a reaction between radical I and benzophenone, leading to benzopinacol and acetone as the final reaction products. The mechanism of this reaction is discussed.

Prolonged irradiation of  $M_I$  results in the formation of a substance ( $M_{II}$ ) with a similar spectrum, which should therefore also be a charge-transfer complex, probably between the radicals I and  $Ph_2\dot{C}-O-C(OH)Me_2$ .

Schenck, Meder and Pape,<sup>1</sup> and Pitts *et al.*,<sup>2</sup> have reported the formation of a highly stable intermediate, possessing a strong long-wave absorption band ( $\lambda_{\max}$  ca. 325  $m\mu$ ), in the photochemical reaction of benzophenone with isopropanol in the absence of oxygen. The same intermediate is formed

under the action of ionizing radiation.<sup>1</sup> Its radical nature is indicated by its reactions with typical radical reagents such as diphenyl-picryl-hydrazyl and nitric oxide.

In the course of work aimed at elucidating the mechanism of the photo-reduction of benzophenone by alcohols,<sup>3</sup> we have been led to undertake a quantitative study of the formation of the above-mentioned coloured reaction product.

## EXPERIMENTAL

### Apparatus and procedure

The solutions to be irradiated were contained in a cylindrical quartz cell with a distance between the end plates of 30 mm and an internal diameter of 21.5 mm. By means of a ground joint a glass tube with a high-vacuum stopcock and a grease trap could be attached to the inlet tube of the cell. The glass tube carried a second ground joint which enabled the cell to be connected to a high-vacuum system. The degassing of the solution by the conventional freeze-pump-thaw technique, using a mixture of solid carbon dioxide and alcohol as coolant, was generally performed with the solution in the cell, a small magnetic stirrer being used to speed up the attainment of equilibrium between the phases. The same stirrer served to stir the solution during irradiation. In some of the later experiments the solution was degassed in a 100 ml round bottom flask, from which it could be transferred under vacuum to the cell without coming in contact with vacuum grease. This procedure led to considerable evaporation of solvent. The absorbance of the benzophenone solution after degassing was taken as a measure of its true concentration.

Measurements of spectra before and after irradiation were at first performed on a Beckman DU spectrophotometer; later a Bausch and Lomb Spectronic 505 recording spectrophotometer was used. The reference cell contained degassed isopropanol. Air-saturated isopropanol was found to have measurable absorption due to dissolved oxygen from *ca.* 260  $m\mu$ , increasing with decreasing wavelength. In a number of experiments the spectra revealed the presence of impurities, with absorption bands in the region below 300  $m\mu$ , that must have been introduced during the degassing process. However, changing to a vacuum grease of very low volatility, Apiezon L, apparently led to complete elimination of this source of error.<sup>4</sup>

The solutions were irradiated with light of wavelength 253.7  $m\mu$  from a spiral-shaped low pressure mercury arc. Unwanted light was removed by means of a filter combination transmitting only in the region 230–280  $m\mu$  (3 cm of a solution of  $\text{NiSO}_4$ , 15 %, +  $\text{CoSO}_4$ , 12.5 %; 1 cm 0.1 mM 2,7-dimethyl-3,6-diaza-cycloheptadiene perchlorate<sup>5</sup>). A quartz lens (focal length 5 cm) and suitable diaphragms rendered the light approximately parallel. The beam entering the cell had a diameter of 13 mm. The increase in transmission at 253.7  $m\mu$  due to the photochemical reaction was recorded by measuring the relative intensity of the transmitted light at frequent intervals by means of a photomultiplier, RCA 1 P – 28, and a sensitive galvanometer, Norma 251 J. The decrease in transmission at a suitable longer wavelength, due to the formation of the coloured reaction product, was studied in a similar way by passing a light beam of wavelength 334  $m\mu$  at right angles through the cell. For this purpose the line at 334  $m\mu$  from a medium pressure mercury arc was isolated by means of a monochromator. The light beam was focussed on the axis of the cylindrical cell by a plane-convex quartz lens (focal length 10 cm). The diameter of the beam entering the cell was about 2 mm. The emerging beam was rendered parallel by a similar lens and its intensity measured in the same way as for the exciting light. At a later stage of the investigation, transmitted intensities at both wavelengths were recorded simultaneously on a two-channel recorder, Texas "servo-riter". The intensity of the analyzing beam was so low that its photochemical effect could be neglected. Both light sources were run on alternating current stabilized by means of a Sorensen voltage regulator.

For actinometry according to Hatchard and Parker,<sup>6</sup> the cell was filled with 6 mM potassium ferrioxalate solution. The intensity of the exciting light was between 4 and 12 micro-einstein ( $\mu\text{E}$ )  $\text{l}^{-1} \text{min}^{-1}$ .

### Materials

*Benzophenone*, Eastman White Label, was recrystallized three times from aqueous methanol. *Isopropanol*, Baker's Analyzed, was fractionally distilled using a column corresponding to 15 theoretical plates. Only the middle fractions were used. *Potassium ferrioxalate* was prepared as described by Parker.<sup>7</sup> *2,7-Dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate* was prepared according to Schwarzenbach.<sup>8</sup> *Nickel sulfate* and *cobalt sulfate* were purified as described by Bäckström.<sup>9</sup>

### RESULTS

Irradiation of a dilute benzophenone solution in isopropanol leads to a gradual increase in light absorption at 334  $\text{m}\mu$ . The absorbance ultimately reaches a maximum value, which we shall denote by  $A_u$ . On prolonged irradiation the absorbance again decreases, but this is a relatively slow process (see below). Similarly the absorbance at 253.7  $\text{m}\mu$  reaches an approximately constant minimum value,  $(A_u)_{253.7}$ , which at low benzophenone concentrations amounts to about 1/3 of the original absorbance of the solution. Prolonged irradiation results in a slow further decrease in absorbance.

The changes in light absorption during irradiation were preceded by an induction period of variable length, undoubtedly due to remaining traces of oxygen in the solution. By thorough degassing the induction period could be reduced to a few seconds.

We shall begin by presenting some results obtained at very low concentrations of benzophenone ( $c_0 < 2 \times 10^{-5}$  M). In Fig. 1, values of  $A_u$  at 334

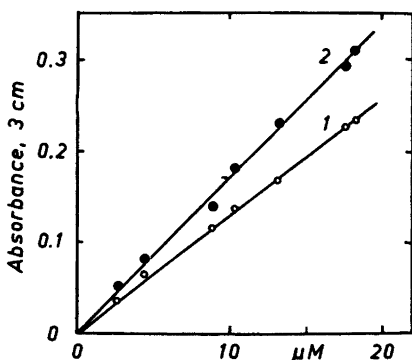


Fig. 1. Absorbance of irradiated benzophenone solutions in isopropanol ( $A_u$ ) vs. their concentrations in  $\mu\text{M}$ . 1, wavelength 334  $\mu\text{m}$ ; 2, wavelength 253.7  $\mu\text{m}$ .

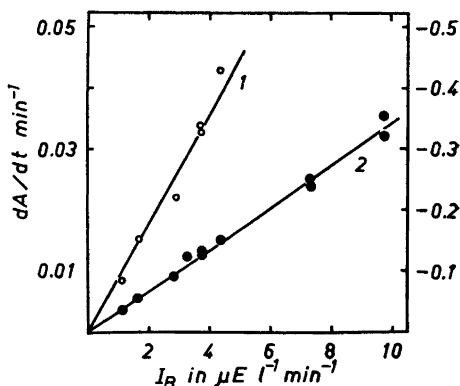


Fig. 2. Initial rate of change of the absorbance of irradiated benzophenone solutions vs. light absorbed by benzophenone  $I_B$ , in micro-einstein  $\text{l}^{-1} \text{min}^{-1}$ . 1, wavelength 334  $\mu\text{m}$ , layer thickness 2.15 cm, scale to the left; 2, wavelength 253.7  $\mu\text{m}$ , layer thickness 3 cm, scale to the right.

and 253.7  $\mu\mu$ , measured at a layer thickness of 3 cm, are plotted *vs.* the initial concentration of benzophenone in  $\mu\text{M}$ . It is evident that the values of  $A_u$  at both wavelengths are approximately proportional to the benzophenone concentration. This indicates that within this concentration range formation of the coloured substance is the only reaction taking place, which is not the case at higher concentrations. The slopes of the straight lines give the following values for its molar extinction coefficient ( $\epsilon \text{ M}^{-1} \text{ cm}^{-1}$ ) at the two wavelengths, calculated per mole of benzophenone consumed in its formation:  $\epsilon_{334} = 4250$ ;  $\epsilon_{235.7} = 5640$ . The corresponding values for benzophenone were found to be 150 and 18 000  $\text{M}^{-1} \text{ cm}^{-1}$ , respectively.

Fig. 2 shows the relation between the initial rate of change of  $A$  and light absorbed by benzophenone ( $I_B$ ) in einstein  $\text{l}^{-1} \text{ min}^{-1}$ . The layer thickness used in measuring  $A$  was 3 cm for 253.7  $\mu\mu$  and 2.15 cm for 334  $\mu\mu$ . The results may be represented by straight lines. From their slopes it may be concluded that only one molecule of benzophenone takes part in the formation of a molecule of the reaction product. The slopes calculated on this basis, assuming that every photoactivated benzophenone molecule reacts with isopropanol, are  $3 \times (5640 - 18\,000) = -37\,100$  and  $2.15 \times (4240 - 150) = 8800$ , respectively. The experimental values are  $-34\,500$  and  $9050$ .

The dependence of the maximum absorbance at 334  $\mu\mu$  of an irradiated benzophenone solution on its initial concentration ( $c_0$ ) is illustrated in Fig. 3 for concentrations up to 100  $\mu\text{M}$ . Experimental values of  $A_u/c_0$ , recalculated to a layer thickness of 1 cm, are here plotted against  $c_0$ . The absorption spectra in the wavelength range 230–380 $\mu\mu$  were practically identical, except for a tendency towards increasing absorption at wavelengths below about 250  $\mu\mu$  with increasing concentration. Light absorption at longer wavelengths was therefore evidently due to the presence of the same substance in all cases, and the absorbance at 334  $\mu\mu$  may be taken as a measure of its concentration. We shall denote this reaction product with  $M_I$ . It is evident from the figure that the yield of  $M_I$  decreases with increasing initial benzophenone con-

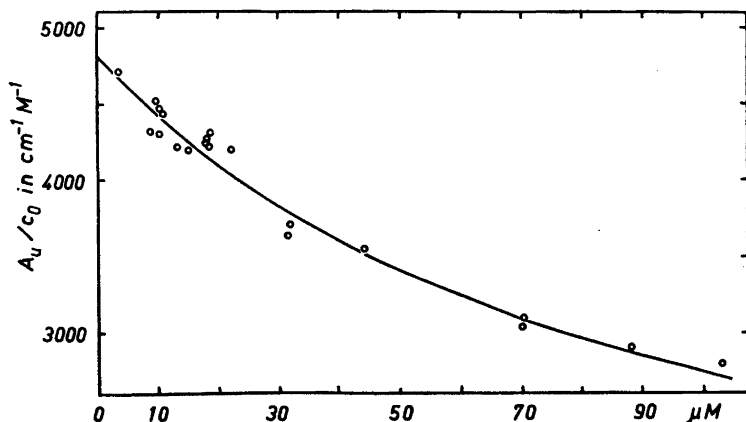


Fig. 3.  $A_u/c_0$  vs.  $c_0$ .  $A_u$  maximum absorbance at 334  $\mu\mu$  and a layer thickness of 1 cm of an irradiated benzophenone solution;  $c_0$  its initial concentration in M.

centration. Extrapolation yields a value of *ca.* 4800 for  $A_u/c_0$  at zero benzophenone concentration, which should be the value of  $\epsilon_{334}$  for  $M_I$ . On the basis of this figure, and the recorded spectra of dilute irradiated solutions, the spectrum of  $M_I$  is reproduced in Fig. 4, curve 1.

The decrease in the yield of  $M_I$  with increasing benzophenone concentration must be due to competition with a reaction in which normal (unexcited) benzophenone molecules take part, and which leads to a reaction product without comparable light absorption in the wavelength region in question, such as benzopinacol. The absorption spectrum of the latter substance is shown in Fig. 4, curve 3. As will be shown below, an attempt at a theoretical treatment of the competing reactions has yielded an equation from which the full-drawn curve in Fig. 3 has been calculated.

It is evident from Fig. 3 that the competing reaction has a noticeable effect on  $A_u$  also at concentrations below 20  $\mu\text{M}$ . The quantum efficiency calculation presented above was therefore based on an assumption which was not altogether correct. For simplicity we shall limit the discussion of this point to the case where the rate of consumption of benzophenone,  $-dc/dt$ , is to be calculated from  $dA/dt$  at 334  $m\mu$ , where  $A$  is the absorbance of the solution. We shall also, for the moment, disregard the relatively weak absorption of benzophenone at this wavelength. The calculation requires a knowledge of  $dA/dc$ . The previous calculation was based on the assumption that  $dA/dc$  was constant during the experiment and, consequently, equal to  $-A_u/c_0$ . In reality, however, since the competing reaction is favoured by a high benzophenone concentration,  $|dA/dc|$  will increase as the benzophenone concentration decreases during the irradiation. Basing a quantum efficiency calculation on the first half of the absorbance curves, which for experimental reasons is to be preferred, and using the approximation  $dA/dc = -A_u/c_0$ , will therefore introduce a systematic error which will make the calculated values too low. Since, as shown by Fig. 3, the above-mentioned theoretical equation may be said to represent the experimental results with fair approximation, it may be used to estimate the magnitude of this systematic error. If only the first 20 % of the curves ( $-\Delta c = 0.2 \times c_0$ ) is utilized for the calculation, the estimated error is 6 % at  $c_0 = 10 \mu\text{M}$  and 12 % at  $c_0 = 20 \mu\text{M}$ . Utilizing a larger portion of the curves for the calculation reduces the errors. The systematic errors to be expected are therefore relatively unimportant at these low concentrations.

Four calculations based on larger portions of the absorbance curves (10–60 % reaction), and with initial benzophenone concentrations in the range 13–18  $\mu\text{M}$ , gave quantum yields for benzophenone consumption ( $\varphi_B$ ) of 1.06, 1.00, 1.03, and 1.01, with an estimated systematic error of  $-4$  %.

It should be mentioned for comparison that previous suggestions as to the composition of the coloured intermediate<sup>1,2,10</sup> would require a value of 2 for  $\varphi_B$ .

#### The effect on $M_I$ of prolonged irradiation

When all the benzophenone in the solution has been consumed, continued irradiation leads to decreasing light absorption. This fact was noted by Pitts.<sup>2</sup>

As shown by our results, the reaction taking place is the formation of a substance having light absorption in the same wavelength region but with a different spectrum. This conclusion is based on the changes in absorbance ( $\Delta A$ ) at different wavelengths produced by continued irradiation. The results of three such experiments are presented in graphical form in Fig. 5, where  $\log(\Delta A) + n$  is plotted *vs.* the wavelength in  $m\mu$ . In order to facilitate comparison, the values of  $n$  have been chosen so as to bring the curves sufficiently close together. Inspection of the figure shows that, within limits of error, the curves are identical in shape in the region 380–290  $m\mu$ .

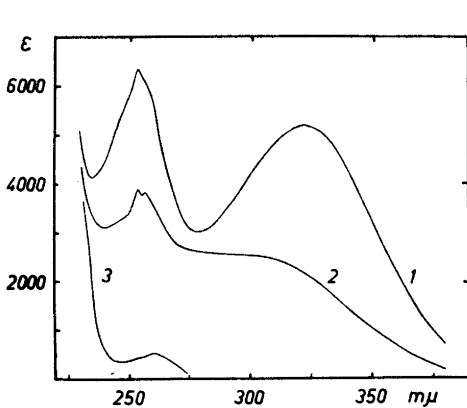


Fig. 4. Molar extinction coefficient,  $\epsilon M^{-1}$  *vs.* wavelength in  $m\mu$ . 1,  $M_I$ ; 2,  $M_{II}$ ; 3, benzopinacol. Values of  $\epsilon$  calculated per mole of benzophenone consumed in the formation of the compound in question.

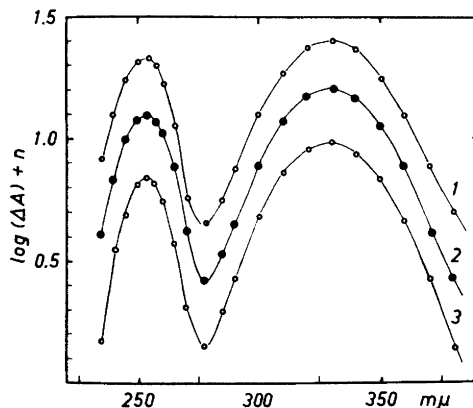


Fig. 5.  $\log(\Delta A) + n$  *vs.* wavelength in  $m\mu$ .  $\Delta A$  = decrease in absorbance of the solution resulting from the photochemical transformation of  $M_I$  into  $M_{II}$ . Layer thickness 3 cm. 1,  $c_0 = 10.3 \mu M$ , 55% transformation,  $n = 2.7$ ; 2,  $c_0 = 18.7 \mu M$ , 100% transformation,  $n = 2$ ; 3,  $c_0 = 103 \mu M$ , 67% transformation,  $n = 1.4$ .

Since the difference-spectrum has its maximum at 330  $m\mu$  as against *ca.* 322  $m\mu$  for  $M_I$ , prolonged irradiation produces not only a lowering of the absorbance in the long-wave band but also a progressing displacement of its maximum towards shorter wavelengths. The final stage of the process is shown in Fig. 4, curve 2. The substance with this absorption spectrum we denote by  $M_{II}$ .

Below 290  $m\mu$  the  $\log(\Delta A)$  curves are still very similar, but there are minor quantitative differences. The impression is gained that the transformation of  $M_I$  into  $M_{II}$  dominates the spectral changes also in this wavelength region, but that also some other reaction may have been taking place to some extent during the period of prolonged irradiation, *e.g.* the decomposition of a hemiketal with formation of the final reaction products (*cf.* Schenck<sup>1</sup>).

Transformation of  $M_I$  into  $M_{II}$  was found to lower the absorbance at 334  $m\mu$  by *ca.* 64.4%. With  $\epsilon_{334} = 4800$  for  $M_I$ , this gives a corresponding value for  $M_{II}$  of 1710, calculated per mole of benzophenone consumed in its

formation. This figure has been used in drawing curve 2 in Fig. 4, which represents the results of an experiment with  $c_0 = 18.7 \mu\text{M}$ .

Knowing the values of  $\epsilon$  for both substances at 334 and 253.7  $m\mu$ , it is possible to calculate the quantum yield of the transformation of  $M_I$  into  $M_{II}$ . The incident light intensity is known and values of absorbance at the two wavelengths are obtained from the recorded transmission curves. Utilizing data from the initial stages of the transformation, where the exciting light is absorbed mainly by  $M_I$ , values of  $\phi$  from 0.07 to 0.09 were obtained, without any apparent concentration dependence. The concentrations of the original benzophenone solutions ranged from 10 to 100  $\mu\text{M}$ .

### DISCUSSION

*Nature of  $M_I$  and  $M_{II}$ .* It is now generally agreed that the primary products formed in the reaction between isopropanol and a photoactivated benzophenone molecule are the radicals  $\text{Me}_2\dot{\text{C}}\text{OH}$  (I) and  $\text{Ph}_2\dot{\text{C}}\text{OH}$  (II). We have shown above that only one benzophenone molecule, namely, the one that has absorbed a light quantum, is consumed in the formation of a molecule of  $M_I$ . In the limiting case of extreme dilution,  $M_I$  is the only stable reaction product formed. Under our experimental conditions its stability seemed to be limited only by air leaking into the system. In one case the absorbance at 334  $m\mu$  decreased by only 5 % in 21 h.

As mentioned in the introduction, the "coloured intermediate" has certain chemical properties in common with free radicals. In other respects its properties are quite different from those of the radicals from which it must have been formed.\*

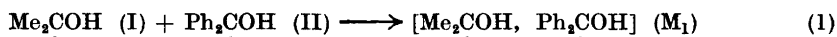
As reported by Porter and Wilkinson,<sup>11</sup> solutions of benzophenone in 50/50 isopropanol + water when subjected to flash photolysis exhibit a transient absorption spectrum that they attribute to the ketyl radical II. It has one maximum at 545  $m\mu$  and another at *ca.* 330  $m\mu$ . From measurements by Beckett and Porter<sup>12</sup> of the rate of decay of the same spectrum in pure isopropanol solution it may be concluded that no measurable light absorption can be ascribed to free ketyl radicals under our conditions.

All that is known about radical I in these respects seems to be that in aqueous isopropanol solution it absorbs in the ultraviolet from about 300  $m\mu$ , and that the absorbance increases with decreasing wavelength.<sup>13</sup>

It is hardly necessary to point out that the properties of  $M_I$  are not those of the mixed pinacol  $\text{Me}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Ph}_2$  which might be formed from radicals I and II. The absorption spectrum of this substance is similar as regards both position and intensity to that of benzopinacol, shown in Fig. 4.

\* The rate of the reaction of  $M_I$  with oxygen is far from being diffusion controlled. This was shown by experiments where the cell was opened after the irradiation and oxygen bubbled through the solution. The decrease in absorbance at 334  $m\mu$  gave a measure of the reaction rate. When the exciting light was again turned on the rate increased > 20 times.

We conclude from the above that  $M_I$  must be a complex, probably of charge-transfer character, formed from radicals I and II. We shall write its formula simply as in eqn. (1):



Such complexes between molecules, *e.g.* between benzene and iodine, are known in great number. It is characteristic of such complexes that their absorption spectra exhibit a strong long-wave band which is not found in the spectrum of either component. These characteristic absorption bands are always very broad and without vibrational fine structure, just as is the case with the long-wave absorption band of  $M_I$ . These features of the absorption band have been ascribed to the looseness of the bonding in the ground state of the complex which allows considerable relative motions of the components.

On the theory of Mulliken,<sup>14,15</sup> the complexes in question are charge-transfer complexes, also called donor-acceptor complexes, in which the primary binding force is due to partial transfer of an electron from the donor to the acceptor. The theory was developed primarily to account for complex formation between molecules, but in the third of his papers on molecular compounds and their spectra,<sup>16</sup> Mulliken indicated the possibility of similar complex formation also between two free radicals. The radical expected to act as donor is described as a system with relatively easily ionized odd electron, the acceptor as an odd-electron system with relatively high electron affinity.

A charge-transfer (CT) complex formed from two different free radicals has not previously been reported in the literature. The formation at low temperatures of complexes between two identical free radicals, described by Hausser and Murrell for certain aromatic nitrogen-containing radicals,<sup>17</sup> represents an altogether different case. The dimers are assumed to be stabilized only by interaction of  $\pi$  electrons of the two fragments.

On Mulliken's theory it is to be expected that two free radicals may form a CT complex only if they are essentially different as regards electron affinity and ionization potential. It is significant, therefore, that in the present case one of the radicals is aliphatic and the other aromatic, and that a CT complex is formed instead of a mixed pinacol. On the other hand, two radicals I may unite to form pinacol,  $\text{Me}_2\text{C}(\text{OH})\text{C}(\text{OH})\text{Me}_2$ . As pointed out by Schenck,<sup>1</sup> this may be concluded from the results obtained by Ciamician and Silber on irradiating a mixture of acetone and isopropanol.<sup>18</sup> Similarly we find that no CT band appears when a solution of benzophenone + benzhydrol in benzene is irradiated, in which case primarily two radicals II are formed.

The following discussion, which must necessarily involve a certain amount of guesswork, will be based on the assumption that no CT complex between two free radicals is to be expected when both are aromatic.

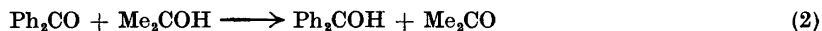
The substance formed from  $M_I$  under the action of ultraviolet light has a spectrum indicating that it must also be a CT complex. The best guess as to its composition seems to be that it may be represented by the formula  $[\text{Me}_2\dot{\text{C}}(\text{OH}), \text{Ph}_2\text{COC}(\text{OH})\text{Ph}_2]$ . If this is correct, the net reaction taking place during the irradiation is:  $2 M_I = M_{II} + \text{Me}_2\text{CHOH}$ . We shall not try to suggest a mechanism for this reaction. It is to be noted, however, that accord-



ing to Mulliken's theory the excited state of  $M_I$  must be largely ionic in character. If dissociation takes place it may therefore be into ions instead of radicals, in that case probably into  $I^+$  and  $II^-$ . The low quantum yield shows that excitation of  $M_I$  in  $> 9$  cases out of 10 leads to no net reaction.

If the formula of  $M_{II}$  is that assumed above, the values of its molar extinction coefficient at different wavelengths will be twice those used in drawing its spectrum in Fig. 4 (curve 2). This will make the intensity of its long-wave absorption band comparable to that of  $M_I$ .

*The competing reaction with benzophenone.* As regards the reaction which leads to decreasing yield of  $M_I$  with increasing benzophenone concentration, certain reactions between benzophenone and radicals I and II have already been suggested as playing an important part in the photochemical formation of benzopinacol from benzophenone and isopropanol. Pitts<sup>2</sup> and Franzen<sup>10</sup> have postulated the following reaction:

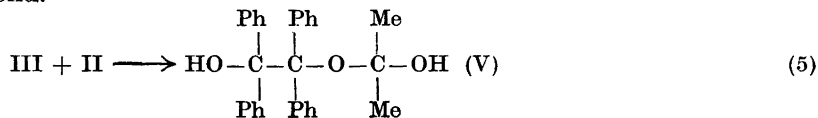


On the other hand, the following two reactions have been suggested by Schenck,<sup>1</sup> as an alternative also by Pitts:<sup>2</sup>



Reactions of the type represented by (3) and (4), where a free radical adds to a carbonyl double bond, are known from the literature.<sup>19</sup> Furthermore, reaction (2) seems unable to account for the evidently very complex nature of the reaction at high benzophenone concentrations. We shall therefore assume that reactions (3) and (4) are those actually occurring.

Reaction (3) transforms radical I into an aromatic radical, whose subsequent reaction with the remaining radical II should result in the formation of a covalent bond.



The reaction product (V) is a hemiketal which may be expected to split into benzopinacol and acetone.

Reaction (4) may be expected to lead to the formation of a CT complex between the aliphatic radical I and the new aromatic radical IV. Evidently this complex would be identical with  $M_{II}$  if the formula we have proposed for this substance is correct. Reaction (4) should therefore result not only in a decrease in the absorbance at  $334 \text{ m}\mu$ , but also in a change in shape of the long-wave absorption band (*cf.* p. 1560).

We thus reach the conclusion that our results can only be explained on the basis of reaction (3). Reaction (4) may also take place but only if its rate is lower than that of (3). A further condition must be that formation of  $M_I$  from radicals I and II is favoured before reactions between I and radicals III and IV.

A further experimental fact which demands an explanation is that the reaction:  $I + I \rightarrow$  pinacol does not take place to a measurable extent. Reaction (1) cannot be assumed to take place within the "cage" of solvent molecules in which the two radicals are formed. This may be concluded, on the basis of theoretical calculations by Noyes,<sup>20</sup> from the facts that the reaction is slow enough to be studied by the flash-photolytic technique,<sup>12</sup> and that a competing reaction with a "scavenger" (benzophenone) has a measurable effect even at concentrations of a few  $\mu\text{M}$ .\* Reaction (1) must therefore be assumed to have a considerably higher rate constant than the reaction leading to pinacol formation. This may be connected with the fact that, although both reactions consist in the formation of a chemical bond, these bonds are of very different kinds. On the theory of Mulliken, one condition for the formation of a CT complex is the overlap of the highest occupied orbital of the donor and the lowest vacant orbital of the acceptor. Other things being equal, a lower ionization potential of the donor and a higher electron affinity of the acceptor should lead to a larger ionic contribution to the ground state and hence to a greater stability of the complex.<sup>21</sup> According to Hausser and Murrell,<sup>17</sup> radicals have both a low ionization potential and a high electron affinity.

As regards the yield of  $M_I$  as a function of the initial benzophenone concentration  $[B]_0$ , it has been pointed out above that reaction (4) must be slower than reaction (3). At low benzophenone concentrations it should therefore be possible to neglect (4) and base the calculation only on reactions (1), (3), and (5). An equation which is in approximate agreement with the experimental results may be derived on the assumption that reaction (3) is reversible and sufficiently rapid for equilibrium to be maintained.



$$-\frac{d[B]}{dt} = \frac{d[M_I]}{dt} + 2 \frac{d[V]}{dt} = k_1 [I] [II] + 2 k_5 [III] [II] \quad (6)$$

$$k_3 [I] [B] = k_{-3} [III] \quad (7)$$

$$-\frac{d[B]}{dt} = \left( k_1 + \frac{2 k_3 k_5}{k_{-3}} [B] \right) [I] [II] \quad (8)$$

$$\frac{d[M_I]}{dt} / -\frac{d[B]}{dt} = k_1 / \left( k_1 + \frac{2 k_3 k_5}{k_{-3}} [B] \right) = \frac{1}{1 + 2\alpha [B]} \quad (9)$$

$$\text{where } \alpha = \frac{k_3 k_5}{k_1 k_{-3}}$$

Integration between the limits  $[B] = [B]_0$ ,  $[M_I] = 0$ , and

$$[B] = 0, [M_I] = [M_I]_{\max}, \text{ gives } [M_I]_{\max} = \frac{1}{2\alpha} \ln (1 + 2\alpha [B]_0) \quad (10)$$

\* Beckett and Porter<sup>12</sup> measured the rate of decay of the transient absorption at 543  $m\mu$  produced by a light flash and calculated a second order rate constant =  $5.9 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ , assuming the reaction to be:  $II + II \rightarrow$  dimer. Our results would indicate that the reaction taking place was essentially  $I + II \rightarrow M_I$ , which would be kinetically undistinguishable from the assumed reaction.

Multiplying  $[M_I]_{\max}$  by the molar extinction coefficient of  $M_I$  at  $334 \mu$  gives the maximum absorbance of the irradiated solution ( $A_u$ ) at this wavelength and a layer thickness of 1 cm. The full-drawn curve in Fig. 3 corresponds to the equation

$$A_u / [B]_0 = \frac{4800}{18\,000 [B]_0} \ln (1 + 18\,000 [B]_0)$$

The available experimental evidence is insufficient to decide whether eqn. (10) is of general validity. Systematic experiments at different light intensities have not yet been performed.

## REFERENCES

1. Schenck, G. O., Meder, W. and Pape, M. *Proc. 2nd U.N. Intern. Conf. Peaceful Uses At. Energy* **29** (1958) 352.
2. Pitts, J. N., Letsinger, R. L., Taylor, R. P., Patterson, J. M., Recktenwald, G. and Martin, R. P. *J. Am. Chem. Soc.* **81** (1959) 1068.
3. Bäckström, H. L. J. *The Svedberg 1884-1944*, Almqvist & Wiksells Boktryckeri, Uppsala 1944, p. 45.
4. Dubois, J. T. and Wilkinson, F. *Appl. Spectry.* **18** (1964) 27.
5. Kasha, M. *J. Opt. Soc. Am.* **38** (1948) 929.
6. Hatchard, C. G. and Parker, C. A. *Proc. Roy. Soc. A* **235** (1956) 518.
7. Parker, C. A. *Ibid.* **220** (1953) 104.
8. Schwarzenbach, G. and Lutz, K. *Helv. Chim. Acta* **23** (1940) 1139; Schwarzenbach, G. and Felder, E. *Ibid.* **27** (1944) 576.
9. Bäckström, H. L. J. *Arkiv Kemi* **13 A** (1940) No. 24.
10. Franzen, V. *Ann.* **633** (1960) 1.
11. Porter, G. and Wilkinson, F. *Trans. Faraday Soc.* **57** (1961) 1686.
12. Beckett, A. and Porter, G. *Ibid.* **59** (1963) 2038.
13. Gordon, S., Hart, E. J. and Thomas, J. K. *J. Phys. Chem.* **68** (1964) 1262.
14. Mulliken, R. S. *J. Am. Chem. Soc.* **74** (1952) 811.
15. Mulliken, R. S. and Person, W. B. *Ann. Rev. Phys. Chem.* **13** (1962) 107.
16. Mulliken, R. S. *J. Phys. Chem.* **56** (1952) 801.
17. Hausser, K. H. and Murrell, J. N. *J. Chem. Phys.* **27** (1957) 500.
18. Ciamician, G. and Silber, P. *Ber.* **44** (1911) 1280.
19. Walling, C. *Free Radicals in Solution*, John Wiley and Sons, New York 1957, p. 283.
20. Noyes, R. M. *J. Am. Chem. Soc.* **77** (1955) 2042.
21. Orgel, L. E. *Quart. Rev. (London)* **8** (1954) 422.

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