Kinetics of Radical Reactions between Methyl, Acetyl and Dimethylamino Radicals Formed in the Flash Photolysis of N,N-Dimethylacetamide in the Gas Phase

Jorma Seetula, Kurt Blomqvist, Kaarlo Kalliorinne and Jouko Koskikallio*

Physical Chemistry Laboratory, University of Helsinki, Meritullinkatu 1C, SF-00170 Helsinki, Finland

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On flash photolysis of N,N-dimethylacetamide in the gas phase, methyl, acetyl and dimethylamino radicals are formed. The final products were analysed by gas chromatography. The rate constants for radical combination and hydrogen-exchange reactions were calculated by a computer integration program using a least-squares iteration method. The hydrogen-donating ability of the radicals increases in the order of increasing electronegativity of the carbon, nitrogen or oxygen atoms of the radicals.

Radical-radical addition reactions usually occur with approximately unit collision efficiency and zero activation energy. A competing hydrogen-transfer reaction between two radicals has been observed in many cases, and in such cases the sum of the reaction rates for radical-radical addition and disproportionation reactions is approximately equal to the collision rate in the gas phase. Khe, Soulignac and Lesclaux[1] obtained the value for the rate constant $k = 1.5 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for the combination reaction of two amino radicals, NH$_2$. Demissy and Lesclaux[2] obtained the value $k = 2.5 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for the combination reaction between an amino and an ethyl radical in the gas phase. No values have been reported for the reactions of dimethylamino radicals in the gas phase. The dimethylamino radical is expected to react with radicals to produce products by addition and also by both hydrogen-donation and -acceptance reactions. In order to study the reaction kinetics for the dimethylamino radical we have photolysed N,N-dimethylacetamide in the gas phase by discharge light flash and determined the reaction products using gas chromatography.

*To whom correspondence should be addressed.

Experimental

Materials. N,N-dimethylacetamide (Fluka AG, puriss.) was purified by vacuum distillation. Dissolved air was removed by freezing the sample to liquid nitrogen temperature, pumping to high vacuum and letting the sample thaw again. This procedure was repeated eight times. Helium (AGA Co.) was used as received. 1,3,5-Trimethylhexahydro-1,3,5-triazine was synthesized according to Ref. 3.

Methods. A 200 cm long quartz reactor with a diameter of 9 mm was placed parallel to a similar flash-lamp quartz tube and both were surrounded by a metal cylinder covered on the inside with a reflecting magnesium oxide layer. The reactor was electrically heated and the temperature was kept constant within ca. 2 K. A 14.7 µF capacitor was connected to the flash lamp and charged at approx. 16 kV, producing an approx. 900 J flash of about 20 µs half-width. The reactor was connected to an Aerograph 1520-1B gas chromatograph with a TC-detector and a 2 cm^2 gas inlet system. Peak areas were measured with a Luxor ABC 800 microcomputer. A 355 cm long glass column with a 1/16″ diameter was filled with 80/100 mesh Chromosorb 103 and was used for ana-

lysing the reaction products. The products were identified by comparing the retention times with those of known samples. One of the products, acetone, was used as a reference, since only relative amounts of products were needed for calculations. Approx. 130 Pa of N,N-dimethylacetamide was introduced into the reactor and ca. 100 kPa of helium was added. The reaction products were analyzed after a total of 1, 2, 4 and 8 flashes and the results were extrapolated to correspond to the amounts of products produced by one flash (see Table 1). From the amounts of products determined the amounts of methyl, acetyl and dimethylamino radicals were calculated. The rate equations for reactions 5–13 were integrated using a computer program.

The calculations were based on the value[4] $k_5 = 2.70 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for reaction 5, in order to obtain values for rate constants comparable with our earlier measurements. If a different value of k_5 is preferred the rate constants should be multiplied by the ratio of the new k_5 value to that used in this work. The mean value ($2.79 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}) of nine different values for the rate constant k_5 reported previously[5] is close to the value which we have used in this work. Since the amount of N,N-dimethylacetamide produced in the combination of acetyl and dimethylamino radicals cannot be measured, the rate constant for reaction 10 was estimated to be $k_{10} = 1.0 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1}.

The values for the rate constants in Table 2 were obtained using a least-squares iteration program. Only two of the rate constants were iter-

ated because they could not be calculated directly from the amounts of products by combining the rate equations. The experimental error in the amount of a product causes an equal relative error in the rate constant for the reaction by which the product was formed, and affects only slightly the values for rate constants of other reactions. The errors in the rate constants shown in Table 2 are calculated from the errors in material balance and estimated errors in product analyses by gas chromatography.

Since all the reactions studied have close to unit collision efficiency, the activation energies are approximately zero. We therefore used in the calculations mean values of amounts of products obtained at different temperatures. After the publication of a preliminary report,[6] additional experiments have been performed and new values for the rate constants calculated.
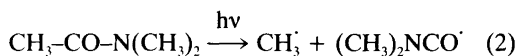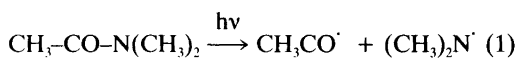
Discussion

The amounts of products formed in the flash photolysis of N,N-dimethylacetamide in the gas phase are shown in Table 1. In addition to the products shown in Table 1, ethene was obtained at a level which was less than 1 % of the amount of ethane. The amounts of products obtained in the reactions between radicals decreased to less than 1 % when 2.66 kPa of NO was added to N,N-dimethylacetamide in the flash experiment. The products obtained in the flash experiments were all formed by reactions between radicals: As a result of the high radical concentrations

Table 1. Relative amounts of products produced in the flash photolysis of N,N-dimethylacetamide in the gas phase at different temperatures in the absence and presence of helium.

T/K	298	296	346	396	
He/kPa	0	100	100	100	
					Mean value
CO	400	480	520	460	465±50
CH$_4$	55	51	57	50	53± 7
C$_2$H$_6$	120	158	196	131	149±15
CH$_3$CHO	265	179	104	88	159±60
CH$_3$COCH$_3$	100	100	100	100	100
(CH$_3$CO)$_2$	32	51	34	20	36± 7
(CH$_3$)$_2$NH		30	29	8	22± 5
(CH$_3$)$_3$N		114	119	118	117±12
((CH$_3$)$_2$N)$_2$		129	122	154	135±13

present in our experiments the radical-radical reactions are much faster than radical-molecule reactions and the latter can therefore be neglected in the calculations.

Photodissociation of N,N-dimethylacetamide is expected to occur by reactions 1 and 2.

$$CH_3-CO-N(CH_3)_2 \xrightarrow{\text{hv}} CH_3CO^{\cdot} + (CH_3)_2N^{\cdot} \quad (1)$$

$$CH_3-CO-N(CH_3)_2 \xrightarrow{\text{hv}} CH_3^{\cdot} + (CH_3)_2NCO^{\cdot} \quad (2)$$

Acetyl radicals contain varying amounts of excess energy and dissociate into a methyl radical and carbon monoxide, or lose their excess energy by collisions.

$$CH_3CO^{\cdot x} \rightarrow CH_3^{\cdot} + CO \quad (3)$$

The dissociation[7] of thermally equilibrated acetyl radicals is slow compared to the rates of radical-radical reactions in our experiments and can thus be neglected.
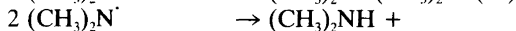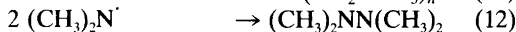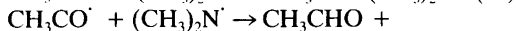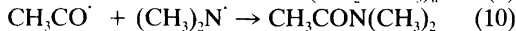
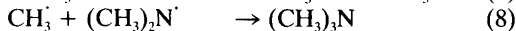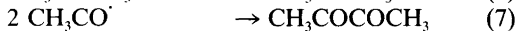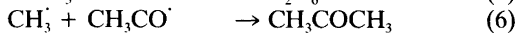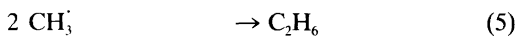The rate constant for the dissociation of the dimethylcarbamoyl radical, $(CH_3)_2NCO^{\cdot}$, is not known. The esr-spectra of this radical have been measured[8] in a solid matrix at 77 K and they indicate that the radical is stable at low temperatures. When studying the flash photolysis of tetramethylurea we observed, among the products, N,N-dimethylacetamide, which we presume to be formed by combination of methyl and dimethylcarbamoyl radicals. This result indicates that thermally equilibrated dimethylcarbamoyl radicals are stable during the radical reactions which take place after the flash photolysis in our experiments. The half-life of the dissociation of dimethylcarbamoyl radicals at 25 K is longer than ca. 10^{-5} s.

$$(CH_3)_2NCO^{\cdot} \rightarrow CO + (CH_3)_2N^{\cdot} \quad (4)$$
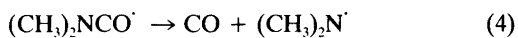
Products such as tetramethylurea, dimethylformamide or methylisocyanate, originating from possible reactions of dimethylcarbamoyl radicals, were not obtained. We conclude that the photodissociation of N,N-dimethylacetamide occurs

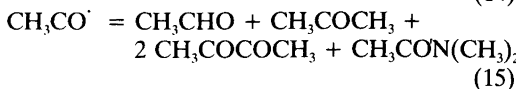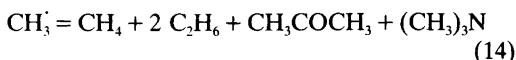via reaction 1 and that reaction 2 is of minor importance, contributing less than about 1%.

The products are assumed to be formed by addition or hydrogen-abstraction reactions between the radicals $CH_3^{\cdot}$, $CH_3CO^{\cdot}$ and $(CH_3)_2N^{\cdot}$ according to reactions 5–13:

$$2\ CH_3^{\cdot} \rightarrow C_2H_6 \quad (5)$$
$$CH_3^{\cdot} + CH_3CO^{\cdot} \rightarrow CH_3COCH_3 \quad (6)$$
$$2\ CH_3CO^{\cdot} \rightarrow CH_3COCOCH_3 \quad (7)$$
$$CH_3^{\cdot} + (CH_3)_2N^{\cdot} \rightarrow (CH_3)_3N \quad (8)$$
$$CH_3^{\cdot} + (CH_3)_2N^{\cdot} \rightarrow CH_4 + 1/n\ (CH_2NCH_3)_n \quad (9)$$
$$CH_3CO^{\cdot} + (CH_3)_2N^{\cdot} \rightarrow CH_3CON(CH_3)_2 \quad (10)$$
$$CH_3CO^{\cdot} + (CH_3)_2N^{\cdot} \rightarrow CH_3CHO + 1/n\ (CH_2NCH_3)_n \quad (11)$$
$$2\ (CH_3)_2N^{\cdot} \rightarrow (CH_3)_2NN(CH_3)_2 \quad (12)$$
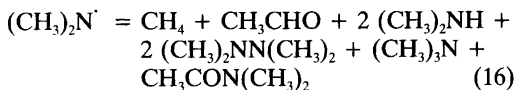$$2\ (CH_3)_2N^{\cdot} \rightarrow (CH_3)_2NH + 1/n\ (CH_2NCH_3)_n \quad (13)$$
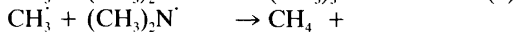
Hydrogen-abstraction reactions of methyl and acetyl radicals to give other radicals are slow and can be neglected. For example, only minor amounts of acetaldehyde and no methane were produced when methyl and acetyl radicals reacted in the flash photolysis of biacetyl in the gas phase at 298 K.[9]

Small amounts of 1,3,5-trimethylhexahydro-1,3,5-triazine, $(CH_3NCH_2)_3$, were produced[10] in the rearrangement of the $CH_2=NCH_3$ product. A polymer, $(CH_3NCH_2)_n$, which is also expected[10] to be formed could not, however, be detected. Jones and Gesser[10] photolysed 6.65 kPa of N,N-dimethylacetamide in the gas phase at 423 K. They obtained most of the products shown in Table 1 except acetaldehyde, acetone and biacetyl. In addition, they obtained small amounts of hydrogen and large amounts of the polymer $(CH_3NCH_2)_n$.

The amounts of the radicals $CH_3^{\cdot}$, $CH_3CO^{\cdot}$ and $(CH_3)_2N^{\cdot}$ formed in the flash photolysis of N,N-dimethylacetamide can be calculated from the relative amounts of products:

$$CH_3^{\cdot} = CH_4 + 2\ C_2H_6 + CH_3COCH_3 + (CH_3)_3N \quad (14)$$

$$CH_3CO^{\cdot} = CH_3CHO + CH_3COCH_3 + 2\ CH_3COCOCH_3 + CH_3CON(CH_3)_2 \quad (15)$$

$$(CH_3)_2N^. = CH_4 + CH_3CHO + 2 (CH_3)_2NH +$$
$$2 (CH_3)_2NN(CH_3)_2 + (CH_3)_3N +$$
$$CH_3CON(CH_3)_2 \qquad (16)$$

According to the material balance the amount of CO ($=465$) should be equal to the amount of $CH_3^.$ ($=568$). Also, the amounts of $CH_3CO^.$ + CO ($=870 + x$) should be equal to the amount of $(CH_3)_2N^.$ ($=717 + x$, where x is the amount of N,N-dimethylacetamide formed in reaction 10, which cannot be measured). The error in the material balance is somewhat larger than expected on the basis of an error of about 10 % in the amounts of reaction products. The formation of small amounts of hydrogen in the flash photolysis of N,N-dimethylacetamide would only slightly decrease the error in the material balance.

In the presence of 100 kPa of helium, radical reactions are assumed to occur between thermally equilibrated radicals. Approximately the same amounts of products were obtained in the presence of 100 kPa of CO_2. When the photolysis of ca. 133 Pa of N,N-dimethylacetamide was carried out in the absence of helium, the amounts of products were only slightly changed (Table 1). The amounts of products obtained at 346 K and 396 K are equal within experimental error to the amounts of products obtained at 296 K. The activation energies for the fast radical-radical reactions are expected to be approximately zero.

From the amounts of products we calculated that about 4–8 % of N,N-dimethylacetamide is photodissociated in one flash. At least 53 % of the photodissociation of N,N-dimethylacetamide occurs by reaction 1, as calculated from the amount of the acetyl radical $CH_3CO^.$ (Eqn. 15). The photodissociation reaction 2 is, however, negligible and the photodissociation of N,N-dimethylacetamide must therefore occur mainly by reaction 1, since no products of dimethylcarbamoyl radical reactions were observed and we have shown by flash photolysis of tetramethylurea that the dimethylcarbamoyl radical is stable during flash experiments. Nicholls and Leermakers[11] found that N,N-dimethylacetamide photodissociates by reactions 1 and 3 at 321 K in cyclohexane or dioxane when using 253.7 nm light. Tilquin, Massaut and Claes[12] have measured the esr spectra of acetyl and dimethylamino radicals formed in the radiolysis of N,N-dimethylacetamide in a solid matrix at 77 K. The dimethylcarbamoyl radical, $(CH_3)_2NCO^.$, was, how-

Table 2. Values of rate constants for the reactions 5–13, calculated from the amounts of products obtained in the flash photolysis of N,N-dimethylacetamide in the gas phase.

Reaction	10^{-10} k/dm³ mol⁻¹ s⁻¹ This work[a]	Previous values	Ref.
5	(2.70)	2.70	4
6	2.75±0.6	3.30[b]	17
		2.98[b]	7
		7.5[b]	18
7	1.50±0.3	2.43[b]	7
		4.5[b]	18
		2.37[b]	17
8	1.75±0.4		
9	0.79±0.2		
10	(1.00)		
11	3.67±0.7		
12	1.67±0.3		
13	0.27±0.06		

[a]Values based on $k_5 = 2.70 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹ and $k_{10} = 1.00 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹. [b]Value based on $k_5 = 3.2 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹.

ever, observed[6] on photolysis of N,N-dimethylformamide at 77 K.

The bond dissociation energy of reaction 1, $\Delta H_1^\circ = (385\pm5)$ kJ mol⁻¹, was calculated using the values[13-15] $\Delta H_f^\circ(CH_3CO) = (-17.0\pm2)$ kJ mol⁻¹, $\Delta H_f^\circ((CH_3)_2N) = (164.1\pm4)$ kJ mol⁻¹ and $\Delta H_f^\circ(CH_3CON(CH_3)_2) = (-238.1\pm2)$ kJ mol⁻¹. From the absorption spectrum of N,N-dimethylacetamide the 0,0 excitation wavelength is estimated to be about 240 nm, corresponding to 498 kJ mol⁻¹. The excess energy of acetyl and dimethylamino radicals formed by the photodissociation reaction 1 is about (113 ± 10) kJ mol⁻¹. The activation energy for the dissociation of the acetyl radical by reaction 3 is[16] 91.2 kJ mol⁻¹. It is therefore not unexpected that about half of the acetyl radicals formed by one flash dissociate by reaction 3.

The rate constants for reactions 6–9 and 11–13 were calculated by computer integration of the rate equation. The calculations were based on the value[4] $k_5 = 2.70 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹ (Table 2). In order to calculate the amount of N,N-dimethylacetamide formed by reaction 10, an estimated value of $k_{10} = 1.00 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹ was used. The calculated value of $k_{11} = 3.67 \cdot 10^{10}$ dm³ mol⁻¹ s⁻¹ is close to the hard sphere collision rate and k_{10} is therefore expected to be small. If, on the

Table 3. Ratios of the rate constants for hydrogen disproportionation reactions and addition reactions with the methyl radical, for radicals in the gas phase.

	HCO˙	CH$_3$O˙	(CH$_3$)$_3$C˙	(CH$_3$)$_2$N˙	CH$_3$CO˙
k_{dis}/k_{add}	5.8	1.5	0.8	0.45	0.05
Ref.	5	5, 17	5	This work	5

other hand, a value of $k_{10} = 0$ was chosen for the calculations, the values of all the other calculated rate constants would increase by about 15 %.

The value of the rate constant k_6 obtained in this work is approximately equal to, and k_7 is smaller than, the corresponding values reported previously (Table 2). The value of $k_8 + k_9 = 2.54 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} is approximately equal to the hard sphere collision rate, whereas $k_{10} + k_{11} = 4.67 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} is somewhat larger and $k_{12} + k_{13} = 1.94 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} is smaller than the collision rate. Owing to long-range dipolar interactions, simple hard-sphere collision rate calculations give only a rough estimate of the collision frequency. The value of $k_{12} = 1.67 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for the radical combination reaction 12 of two dimethylamino radicals is close to the value[1] $k_{12} = 1.5 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for the combination reaction of two amino radicals NH$_2$˙. The value $k_8 = 1.75 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} for the combination of methyl and dimethylamino radicals is smaller than the rate constant $k = 2.5 \cdot 10^{10}$ dm^3 mol^{-1} s^{-1} obtained[2] for the combination reaction of ethyl and amino radicals.

The hydrogen-donating ability of the dimethylamino radical is close to that of the *tert*-butyl radical, as measured by the ratio of rate constants for disproportionation reactions and addition reactions of these radicals with a methyl radical (Table 3). The HCO˙ and CH$_3$O˙ radicals are the most effective hydrogen donors, and the acetyl radical CH$_3$CO˙ is the least effective, when compared with the dimethylamino radical. Excluding

the carbonyl radicals, the order of the hydrogen-donating reactivity of radicals increases approximately in the order carbon, nitrogen and oxygen, which is the order of increasing electronegativity. The hydrogen-donating ability of acetyl, methyl and dimethylamino radicals decreases in that order, as measured by the ratio of rate constants for disproportionation and addition reactions of the radicals (Table 4). The hydrogen-accepting ability of these radicals decreases in the order of increasing electronegativity of carbon, nitrogen and oxygen, which is the reverse of the order of hydrogen-donating ability (Table 4).

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Table 4. Ratios of the rate constants for hydrogen disproportionation reactions and addition reactions with the dimethylamino radical, for radicals in the gas phase.

	CH$_3$CO˙	CH$_3$˙	(CH$_3$)$_2$N˙
k_{dis}/k_{add}	(3.7)	0.45	0.16

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