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ON THE REACTIONS OF "HOT" METHYL RADICALS IN THE SOLID PHASE AT LOW TEMPERATURES

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In studying the photolysis of such compounds as CH_3J, $CH_3N_2CH_3$, and $(CH_3)_2Hg$ in the gas phase, a number of works (1-5) proposed the formation, in the primary act of photolysis, of "hot," i.e., excess-energy-containing, methyl radicals. This proves possible in the case when the energy of the absorbed light quantum substantially exceeds the energy of the bond being broken. The conclusion that "hot" radicals are formed was drawn on the basis of the fact that the yield of methane in the reaction $CH_3\cdot + RH \rightarrow CH_4 + R\cdot$ either does not depend on temperature, or this dependence does not obey the Arrhenius law. The question of "hot" methyl radicals has been studied in greatest detail in the case of methyl iodide (2, 3), although there are also certain indications of their formation in the photolysis of other compounds (4, 5).

[Figure 1 diagram]

Fig. 1. Diagram of the apparatus for irradiation with ultraviolet light at 77° K

Very little is known about the photolysis of the above-listed compounds in the solid phase. We may mention the work of Mador (6), who found CH_4, C_2H_6, C_2H_4, and CH_2J_2 among the photolysis products of CH_3J at the temperature of liquid helium. Upon irradiation with X-rays of methyl iodide (7) and dimethylzinc (8) frozen at 77° K, methyl radicals were identified by the method of electron paramagnetic resonance (EPR) (9, etc.).

The purpose of the present work was to study the transformations and stabilization conditions of methyl radicals obtained by photolysis of methyl iodide, azomethane, acetone, and acetaldehyde at 77° K, and to elucidate the role of "hot" radicals in these processes. In solving this problem we used both data from analysis of the gaseous reaction products and EPR data.

Transparent solid solutions of the compounds under study in methylcyclohexane were subjected to photolysis. The concentration of the solutions was 0.02–0.15 mole/liter. Irradiation was carried out with a PRK-7 mercury lamp in a quartz vessel cooled with liquid nitrogen (Fig. 1). Before irradiation the solutions were thoroughly evacuated. After irradiation, the fraction containing methane and nitrogen was separated from the solution by thawing it and refreezing to −196° C, after which the ethane fraction, which did not freeze at −130–140° C, was isolated in an analogous manner. The gas pressure was measured with a membrane manometer. The ratio between methane and nitrogen was determined mass-spectrometrically.

For investigation of the radicals formed by the EPR method, the evacuated solution was irradiated at 77° K in quartz ampoules 2–3 mm in diameter, which were then transferred without thawing from the Dewar vessel with liquid

azomethane, placed in the resonator of an EPR-2 instrument described in work (^{9}).

In separate experiments a BS-5 filter was used, transmitting light with $\lambda > 3100$ Å, and a filter filled with a mixture of $Cl_2 + Br_2$, transmitting light with $\lambda < 2900$ Å.

The data obtained by us show that during photolysis of azomethane in the solid phase, nitrogen is formed predominantly; the number of its molecules is equal to the number of decomposed azomethane molecules, and ethane is formed in an amount equal, within the accuracy of the measurements, to the amount of nitrogen. Methane was also found among the reaction products. The ratio CH_4/C_2H_6 is ~ 0.04 and does not depend on the light intensity. The only gaseous product of photolysis of CH_3J is methane. Under the conditions of our experiments, acetone does not decompose, while acetaldehyde decomposes only slightly into CO and CH_4, which are formed in approximately equal amounts.

The decomposition of azomethane in the solid phase probably occurs in the same way as in the gas reaction according to

$$CH_3N_2CH_3 \rightarrow 2CH_3 \cdot + N_2.$$

The formation of ethane during photolysis of azomethane may occur both as a result of recombination of methyl radicals freely diffusing in the matrix and as a result of their recombination inside the "cage." However, only in the first case should the ratio CH_4/C_2H_6, as a simple calculation shows, have depended on the light intensity. The data given above indicate that during photolysis of azomethane the radicals recombine mainly inside the "cage."

Table 1

Experiment No.	Photolysis conditions	CH_4/C_2H_6
1	Unfiltered light	0.035
2	Unfiltered light	0.047
3	Unfiltered light	0.042

Experiment No.	Photolysis conditions	CH_4/C_2H_6
4	With BS-5 filter$\lambda > 3100$ Å	0.020
5	With BS-5 filter$\lambda > 3100$ Å	0.016
6	With $Cl_2 + Br_2$ filter$\lambda < 2900$ Å	0.14
7	With $Cl_2 + Br_2$ filter$\lambda < 2900$ Å	0.14

The formation of methane during photolysis of methyl iodide and azomethane indicates that even at 77° K the reaction of abstraction by a methyl radical of a hydrogen atom from solvent molecules, whose activation energy in the gas phase is 6-9 kcal/mole, proceeds at an appreciable rate. These facts can be explained by the assumption that "hot" methyl radicals are also formed during photolysis of these compounds in the solid phase.

It is known that the photochemical decomposition of acetone in the gas phase at temperatures below 100° C proceeds with rupture of one of the $C-CH_3$ bonds ([1]). The stability of acetone under photolysis in the solid phase indicates the absence, in contrast to CH_3J, of "hot" methyl radicals. This is connected with the fact that the C–C bond energy in acetone (77 kcal/mole) ([7]) is much greater than the C–J bond energy in methyl iodide (54 kcal/mole), while the mass of the $CH_3CO\cdot$ radical is much less than the mass of an iodine atom. Apparently, the radicals $CH_3\cdot$ and $CH_3CO\cdot$ formed in the primary act of acetone photolysis recombine in the overwhelming majority of cases into the starting molecule. The formation of CH_4 and CO during photolysis of acetaldehyde may be connected either with its intramolecular decomposition according to the reaction

$$CH_3CHO \rightarrow CH_4 + CO,$$

or with disproportionation of the radicals formed in the primary act:

$$CH_3CHO \rightarrow CH_3 \cdot + CHO\cdot,$$

$$CH_3 \cdot + CHO\cdot \rightarrow CH_2 + CO.$$

To confirm the assumption concerning the participation of "hot" methyl radicals in the reaction of methane formation, photolysis of azomethane was carried out with light in different wavelength intervals. The corresponding data are given in Table 1. The fact that changing the wavelength from $\lambda < 2900$ Å to

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

$\lambda > 3100$ Å led to a sevenfold increase in the CH_4/C_2H_6 ratio, confirms the assumption that methane is formed from "hot" methyl radicals, the fraction of which is greater the higher the energy of the absorbed quantum.

Fig. 2 shows the EPR spectrum of radicals formed upon irradiation of CH_3J in methylcyclohexane with unfiltered light from a mercury lamp, and Fig. 3 shows the spectrum of the methylcyclohexyl radical obtained by irradiation with fast electrons of methylcyclohexane frozen at 77° K*. These spectra are very similar to one another. Thus, the spectrum in Fig. 2 belongs to the methylcyclohexyl radical, obtained by abstraction of a hydrogen atom from a methylcyclohexane molecule.

Fig. 2. EPR spectrum of radicals formed upon irradiation of CH_3J in methylcyclohexane with unfiltered light

Fig. 3. EPR spectrum of radicals formed upon irradiation of methylcyclohexane with fast electrons

Fig. 4 shows the spectra of radicals formed upon irradiation of azomethane in a methylcyclohexane medium with unfiltered light from a mercury lamp (Fig. 4 *a*) and with light with $\lambda > 3100$ Å (Fig. 4 *b*). In both spectra four components can be distinguished, with a splitting of ~ 23 oersteds and an intensity ratio approximately equal to $1:3:3:1$, which indicates the presence of methyl radicals in these spectra. The remaining lines, belonging to the methylcyclohexyl radical, occupy the same position in both spectra, but their intensity relative to the lines of the methyl radicals is different. Especially prominent in the spectrum of Fig. 4 *b* are two side lines which are present in Fig. 4 *a* only as small shoulders; the distance between them corresponds to the splitting between the outer lines in Fig. 2. On this basis it may be concluded that in the case (Fig. 4 *b*) the ratio $CH_3/R\cdot$ (where $R\cdot$ is the methylcyclohexyl radical) is smaller than in the case (Fig. 4 *a*).

Fig. 4. EPR spectra of radicals formed upon irradiation of azomethane in methylcyclohexane: *a* —with unfiltered light, *b* —with light with $\lambda > 3100$ Å. Crosses indicate the components of methyl radicals

Fig. 4

Figure 3: Fig. 4

Thus, the methyl radicals obtained in the photolysis of azomethane in the solid phase can: 1) recombine immediately after their formation in the "cage" (formation of C_2H_6), 2) enter into substitution reactions with molecules of the medium (formation of CH_4 and $R\cdot$), 3) become stabilized upon escape from the "cage" (EPR spectrum of CH_3 radicals). The ratio of these pathways depends on the energy of the absorbed light. Its increase leads, first, as noted above, to an increase in the fraction of methyl radicals reacting with

* Irradiation of the sample and recording of the EPR spectrum were carried out on the apparatus of the Institute of Chemical Physics, Academy of Sciences of the USSR, by I. I. Cheidze.

molecules of the medium with the formation of methane, as compared with recombining ones, and, secondly, to an increase in the fraction of CH_3 radicals stabilized with escape from the "cage," as compared with reacting ones. The results obtained thus make it possible to draw an unambiguous conclusion that "hot" methyl radicals are indeed formed during the photolysis of CH_3J and $CH_3N_2CH_3$ in the solid phase. On the other hand, it also follows from these data that the nature of the interaction of these "hot" methyl radicals with molecules of one and the same medium (methylcyclohexane) depends on the structure and bond energies of the molecule decomposing with the formation of the CH_3 radical, and on the wavelength of the light causing this decomposition. Apparently, this effect is associated with differences in the nature of the excitation of "hot" methyl radicals formed by different pathways.

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1. E. W. R. Steacie, *Atomic and Free Radical Reactions*, N. Y., 1954.
2. R. D. Schultz, H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950).
3. R. D. Souffie, R. Williams Jr., W. H. Hamill, *J. Am. Chem. Soc.*, **78**, 917 (1956).
4. W. C. Sleppy, J. G. Calvert, *J. Am. Chem. Soc.*, **81**, 769 (1959).
5. M. K. Phibbs, B. Darwent, *Trans. Farad. Soc.*, **45**, 541 (1949).

6. I. L. Mador, *J. Chem. Phys.*, **22**, 1617 (1954).
7. T. Cole, H. O. Pritchard, N. R. Davidson, H. M. McConnel, *Mol. Phys.*, **1**, 408 (1958).
8. W. Gordy, C. G. McCormick, *J. Am. Chem. Soc.*, **78**, 3243 (1956).
9. A. P. Semenov, N. N. Bubnov, *Problems in Experimental Technique*, No. 1, 92 (1959).
10. N. N. Semenov, *On Certain Problems of Chemical Kinetics*, Publishing House of the USSR Academy of Sciences, 1958.

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