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Studies of Photochemical Reactions Using Organic Photosensitizers. III. Direct Photolysis and Biacetyl-photosensitized Decomposition of Azopropanes

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The direct photolyses in the two wavelength regions and the biacetyl-photosensitized decomposition have been studied for 1,1′-azo-*n*-propane and 2,2′-azo-isopropane. The value of k_d/k_c, the ratio of the disproportionation rate to the combination rate of free radicals, has been found to be slighlty dependent on the exciting wavelength as for *n*-propyl and isopropyl radicals. The higher the exciting energies, the larger the ratio k_d/k_c. From the quenching study of biacetyl phosphorescence, it was found that the energy of the excited biacetyl molecule was transferred to the azopropane molecule at every collision.

The disproportionation and combination of alkyl radicals have been the object of many investigations. In the preceding work on the photodecomposition of vinyl iodide in the gas phase,[1] we found the slight energy dependence of k_d/k_c, the ratio of the rate of disproportionation to that of combination reactions of vinyl radicals as in the case of CH_3S radicals.[2]

In the present work, we have carried out the direct photolyses in the two wavelength regions and the biacetyl-photosensitized decomposition of 1,1′-azo-*n*-propane and 2,2′-azo-isopropane in order to study the energy dependence of the *n*-propyl and isopropyl radicals produced. The effect of the excess energy of *n*-propyl and isopropyl radicals on the ratio of k_d/k_c has been examined.

The photosensitizer, biacetyl, has been used for exciting azopropane to an excited state lower than the excited states caused by direct absorption in the UV-range or by mercury-photosensitization.

In the preceding papers of this series[3,4] we reported the benzene-photosensitized photolysis of nitrous oxide and the biacetyl-photosensitized photolysis of dimethylnitrosoamine, where the reactants were excited to the triplet states lying in the lower level comparing with the excited singlet states produced by direct absorption.

Since the lowest triplet level of biacetyl has been known to be 56 kcal/mol,[5] the *n*-propyl and isopropyl radicals produced by the biacetyl-sensitized photolyses of the corresponding azopropanes should have much less excess energy compared with the case of direct photolyses.

The phosphorescence of biacetyl was found to be quenched effectively[6] by azoalkanes indicating high efficiency of energy transfer from the biacetyl molecule in the triplet state to azoalkane molecules.

Experimental

Azo-*n*-propane and azo-isopropane were obtained from Merck Sharp and Dohme of Canada Ltd. and were purified by vacuum distillation and stored at low temperature in the dark. The absorption spectra of azo-*n*-propane and azo-isopropane in the vapor phase are shown in Fig. 1.

The apparatus was similar to that of the previous work[1] and a high intensity light source, USH-500D high pressure mercury lamp manufactured by Ushio Electric Co., was used for the sake of the predominance of radical-radical reactions with high concentration of the free radicals excluding radical-molecule reactions.[1,7]

For the direct photolysis, Toshiba UV-35 and UV-29 filters were used. When UV-35 was used, 366 nm line of the mercury lamp was almost exclusively effective for the photolyses of both azo-*n*-propane and azo-isopropane. By use of UV-29 filter, about ten percent contribution from 334 nm line was estimated for the excitation of azo-*n*-propane

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[1] S. Yamashita, S. Noguchi, and T. Hayakawa, This Bulletin, **45**, 659 (1972).

[2] A. Jones, S. Yamashita, and F. P. Lossing, *Can. J. Chem.*, **46**, 833 (1968); S. Yamashita and F. P. Lossing, *ibid.*, **46**, 2925 (1968).

[3] S. Yamashita, K. Adachi, and T. Hayakawa, This Bulletin, **43**, 2332 (1970).

[4] S. Yamashita and T. Hayakawa, "Proceeding of the International Conference on Mass Spectroscopy", Kyoto (1969), p. 1113.

[5] H. Ishikawa and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **84**, 1502 (1962); G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

[6] R. E. Rebbert and P. Ausloos, *ibid.*, **87**, 1847 (1965).

[7] J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2317 (1967).

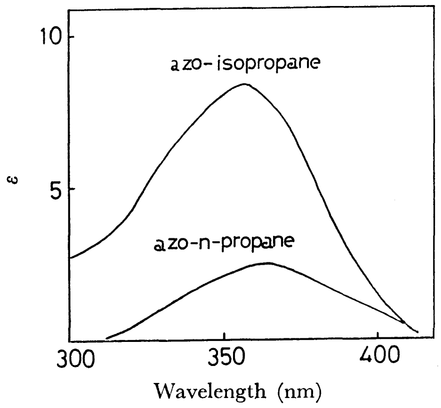

Fig. 1. Absorption spectra of azo-isopropane and azo-*n*-propane.

and about thirty percent contribution from 302, 313, and 334 nm lines for the excitation of azo-isopropane. Highly monochromatic light was not available to excite the reactants because high intensity of the light source was necessary for high concentration of free radicals. All of the runs were carried out at room temperature in the dark room. Before the analysis of the reaction products, unreacted azopropanes were condensed by a cold trap cooled at −20 °C. The separated products were analyzed by a gas chromatograph using a column packed with dimethylsulfolane on alumina, and by a Hitachi RMU-5 mass spectrometer when necessary. The emission measurements for quenching were carried out in the dark room. The exciting light was 436 nm line of a mercury lamp and the phosphorescence emitted by biacetyl in the absence and presence of azopropanes was measured by a grating monochromator and 1P28 photomultiplier with TR-8651 electrometer of Takeda Riken Ind. Co. Ltd.

Results and Discussion

The reaction products obtained were N_2, C_3H_8, C_3H_6, and C_6H_{14} in the direct photolysis and biacetyl-sensitized photolysis of both azopropanes. The product hexane was *n*-hexane in the photolysis of 1,1′-azo-*n*-propane and 2,3-dimethylbutane from 2,2′-azo-isopropane, respectively. In all of the runs, the amounts of C_3H_8 and C_3H_6 were found to be equimolar.

Under high light intensity conditions of this work, the reaction scheme may be rather simplified as following because radical-molecule reactions can be neglected due to the high concentration of the free radicals.

For the direct photolysis, the reaction scheme may be proposed as follows:

$$C_3H_7N_2C_3H_7 + h\nu \longrightarrow C_3H_7N_2C_3H_7^* \qquad (1)$$

$$C_3H_7N_2C_3H_7^* \longrightarrow N_2 + C_3H_7\cdot + C_3H_7\cdot \qquad (2)$$

$$C_3H_7\cdot + C_3H_7\cdot \begin{cases} \xrightarrow{k_d} C_3H_8 + C_3H_6 & (3) \\ \xrightarrow{k_c} C_6H_{14} & (4) \end{cases}$$

For the biacetyl-sensitized photolysis, the following processes seem to produce propyl radicals:

$$B + h\nu' \longrightarrow B^* \longrightarrow B^{**} \qquad (5)$$

$$B^{**} + C_3H_7N_2C_3H_7 \longrightarrow B + C_3H_7N_2C_3H_7^{**} \qquad (6)$$

$$C_3H_7N_2C_3H_7^{**} \longrightarrow C_3H_7\cdot + C_3H_7\cdot + N_2 \qquad (7)$$

here, B means biacetyl and the symbols *, ** denote excited singlet and triplet states, respectively. According to the reaction scheme shown above, equimolar amounts of C_3H_8 and C_3H_6 should be produced, which is supported by the experimental results obtained.

The amount of CO and C_2H_6 were found to be negligible in the biacetyl-photosensitized reaction, meaning that the side reactions of the biacetyl photodecomposition could be left out of account probably because of the extremely large quenching cross section for biacetyl by azopropanes as described later.

Since the greaseless system was not available in the present work, complete separation of hexane has not been achieved. The corrected value of the rate of hexane formation was estimated by the difference $[N_2]-[C_3H_8]$ assuming a material balance between the products as described in the photolysis of 2,2′-azo-isobutane.[8] This procedure for the estimation of hexanes was found reasonable by a blank test and by the fact that the ratio between the direct photolysis products was in good agreement with the results of the greaseless system work reported by Terry and Futrell[7] when the wavelength range for excitation was arranged similar to their conditions.

Table 1. Photolysis of azo-isopropane
Illumination time: 2∼10 min

Filter	Pressure (Torr)	Products (micromole)				k_d/k_c
		N_2	C_3H_8	C_3H_6	C_6H_{14}	
UV-29	20.15	54.50	22.16	21.92	32.34	0.685
	20.18	43.62	18.13	18.30	26.49	0.712
	19.86	25.96	10.77	10.94	15.19	0.709
	20.11	13.96	5.60	5.57	8.36	0.671
UV-35	19.65	46.48	18.00	17.64	28.48	0.631
	19.98	36.40	13.92	15.48	22.48	0.619
	19.95	30.58	11.72	12.31	18.86	0.621
	19.62	21.09	8.22	8.63	12.87	0.639

Table 1 shows the results of the direct photolysis of azo-isopropane using UV-29 and UV-35 filters. The value of k_d/k_c was obtained by taking the ratio $[C_3H_8]/\{[N_2]-[C_3H_8]\}$ equal to $[C_3H_8]/[C_6H_{14}]$ assuming a material balance as described above. Table 2 shows the results of the direct photolysis of azo-*n*-propane.

The amounts of the photolysis products were found to be proportional to the illumination time, which

Table 2. Photolysis of azo-*n*-propane
Illumination time: 2∼10 min

Filter	Pressure (Torr)	Products (micromole)				k_d/k_c
		N_2	C_3H_8	C_3H_6	C_6H_{14}	
UV-29	22.20	9.89	1.23	1.12	8.66	0.143
	20.01	14.89	1.89	1.78	12.92	0.146
UV-35	20.60	25.02	2.80	2.80	22.22	0.126
	20.60	19.48	2.15	2.10	16.33	0.124
	20.10	9.74	1.06	1.03	8.68	0.122
	20.25	27.31	3.01	3.19	24.30	0.124
	20.40	32.00	3.51	3.74	28.49	0.123

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[8] D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **65**, 175 (1969).

TABLE 3. BIACETYL-SENSITIZED PHOTOLYSIS OF AZO-ISOPROPANE

Filter: Toshiba VY-43.
Illumination time: 10~20min

Reactant pressure (Torr)	Biacetyl pressure (Torr)	Products (micromole)				k_d/k_c
		N_2	C_3H_8	C_3H_6	C_6H_{14}	
19.91	27.30	1.75	0.44	0.42	1.33	0.33
19.57	26.80	2.17	0.43	0.48	1.69	0.25
20.28	25.00	0.87	0.17	0.17	0.70	0.24

TABLE 4. BIACETYL-SENSITIZED PHOTOLYSIS OF AZO-*n*-PROPANE

Filter: Toshiba VY-43.
Illumination time: 10~20 min

Reactant pressure (Torr)	Biacetyl pressure (Torr)	Products (micromole)				k_d/k_c
		N_2	C_3H_8	C_3H_6	C_6H_{14}	
20.65	30.58	0.602	0.033	0.033	0.569	0.07
12.98	22.95	1.041	0.046	0.046	0.995	0.05
16.14	22.86	1.014	0.034	0.034	0.980	0.04

means that all the reaction products were produced in the primary process, not in the secondary process.

Tables 3 and 4 show the results of the biacetyl-photosensitized decomposition of azo-isopropane and azo-*n*-propane, respectively. The quantum yields of N_2 formation were obtained for the direct photolysis by UV-35 and for biacetyl-photosensitization, as shown in Table 5. The quantum yields by biacetyl-photosensitization are about one tenth smaller than that by the direct photolysis.

Figure 2 shows the phosphorescence spectrum of biacetyl vapor in the absence and presence of quenchers. Ausloos and Rebbert reported much higher cross sections of azomethane and azoethane than that of oxygen for quenching the phosphorescence of biacetyl.⁶⁾ In the present work azo-isopropane was found to have higher cross section than azomethane for quenching the phosphorescence of biacetyl. From the Stern-Volmer plot of the quenching experiments, the quenching rate constant k_q was found to be 3×10^{11} $\mathrm{l\,mol^{-1}\,s^{-1}}$, equivalent to the value of the effective collisional cross section $\sigma_Q{}^2$ of $45\times10^{-16}\,\mathrm{cm^2}$ taking the lifetime of the excited triplet biacetyl molecule to be 10^{-3} s.⁹⁾ The value of the quenching rate constant k_q suggests that the excited biacetyl molecule is quenched at every collision with azopropane molecule meaning high efficiency of energy transfer from excited biacetyl to reactant azopropane.

TABLE 5. QUANTUMM YIELDS OF N_2 FORMATION OBTAINED BY DIFFERENT EXCITATIONS

Reactants	Direct photolysis with UV-35 (366 nm)	Biacetyl-photosensitization
Azo-isopropane	0.66±0.04	0.08±0.02
Azo-*n*-propane	0.98±0.14	0.06±0.01

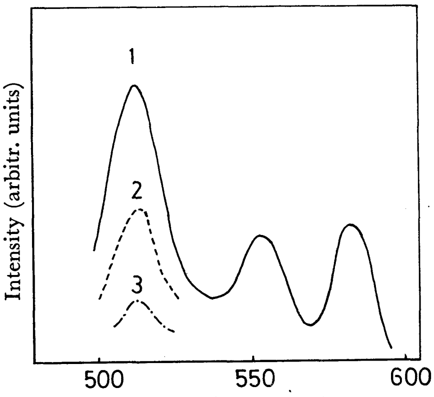

Fig. 2. Phosphorescence of biacetyl vapor (20 Torr, 20 °C). Curve 1: pure biacetyl, Curve 2: with 0.038 Torr O_2, Curve 3: with 3.7×10^{-4} Torr azo-isopropane.

Rather low quantum yield of the azopropane decomposition in the case of the biacetyl-sensitized photolysis, in spite of the high efficiency of energy transfer from excited biacetyl to reactant azopropane, shows that excited azopropane produced by biacetyl-photosensitization is more easily deactivated than by the direct photolysis.

TABLE 6. DEPENDENCE OF THE RATIO k_d/k_c ON THE EXCITATION ENERGIES FOR THE PRODUCTION OF PROPYL RADICALS

Reactant	Excitation condition	Excitation energy (kcal/mol)	k_d/k_c
Azo-isopropane	Direct photolysis (UV-29 filter)	78~95	0.69
	Direct photolysis (UV-35 filter)	78	0.63
	Biacetyl-photosensitization	56	0.27
Azo-*n*-propane	Direct photolysis (UV-29 filter)	78~95	0.15
	Direct photolysis (UV-35 filter)	78	0.12
	Biacetyl-photosensitization	56	0.05

Table 6 summarizes the k_d/k_c values obtained with different excitation energies. The ratio k_d/k_c increases with increasing excitation energies for both azo-isopropane and azo-*n*-propane, which means that k_d/k_c increases with the increment of the excess energies carried by propyl radicals produced by photolysis. This tendency agrees with the results obtained in the case of $CH_2{=}CH\cdot$¹⁾ and $CH_3S\cdot$²⁾ radicals produced by the photolyses.

The processes (2) and (7) forming two propyl radicals and one nitrogen molecule may be composed of two successive one-bond fission steps:

$$C_3H_7N_2C_3H_7{}^* \text{ (or } C_3H_7N_2C_3H_7{}^{**}) \longrightarrow C_3H_7N_2 + C_3H_7 \qquad (8)$$

and succeedingly

$$C_3H_7N_2 \longrightarrow C_3H_7 + N_2 \qquad (9)$$

Such two-step mechanism was previously confirmed

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9) H. L. J. Backström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

in the case of the direct photolysis of azo-*n*-propane by illumination of the molecular flow of the reactant in the ion source of a mass spectrometer.[10)]

The excess energies carried by propyl radicals were estimated in the case of azo-isopropane since the dissociation energy of the C–N bond of azo-isopropane has been found to be about 33 kcal/mol.[11)] From the value of the C–N bond dissociation energy of azo-isopropane and other thermochemical data, the upper limit of the excess energy of the isopropyl radical may be estimated to be 28 kcal/mol for the direct photolysis with UV-35 and 14 kcal/mol for biacetyl-photosensitization. Table 6 shows, anyway, the higher the excitation energies, the larger the excess energies carried by propyl radicals resulting in the increment of k_d/k_c values. The considerably small k_d/k_c values obtained in the biacetyl-photosensitization might suggest the effect of the spin-multiplicity difference besides the energy dependence of k_d/k_c.

Since the effect of the addition of *n*-butane as third body to the reaction system was found almost insignificant, it was inferred that the hot propyl radicals produced by the highly intense illumination reacted each other before thermalization in accord with the suggestion given by Thynne.[12)]

It may be said that the disproportionation reaction of free radicals is a kind of inter-radical hydrogen-atom abstraction in the transition state.[13),14)] From this viewpoint the increment of the k_d/k_c values with increasing excitation energies seems to be understandable since the feasibility of hydrogen-atom abstraction by the free radicals increases with the increment of the excitation energies used for photochemical free radical formation.[15),16)]

[10)] S. Yamashita and T. Hayakawa, This Bulletin, **46**, 2290 (1973).

[11)] B. G. Gowenlock, J. R. Majer, and D. R. Snelling, *Trans. Faraday Soc.*, **58**, 670 (1962).

[12)] J. C. J. Thynne, *Proc. Chem. Soc.*, **1961**, 68.

[13)] J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

[14)] R. J. McNeal, *ibid.*, **40**, 108 (1964).

[15)] P. C. Kobrinsky and R. M. Martin, *ibid.*, **48**, 5728 (1968).

[16)] J. M. White, R. L. Johnson, Jr., and D. Bacon, *ibid.*, **52**, 5212 (1970).