

PHOTOLYSIS OF CHLOROBENZENE SENSITIZED BY KETONES IN SOLUTIONS

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Ketones belong to the group of compounds the photophysical and photochemical properties of which are studied in every respect and have already become quite well known¹⁻⁶⁾. It was found, *inter alia*, that ketones demonstrate photosensitizing properties in regard to many a reaction, both in liquid and in vapor phase. Not all the processes studied, photosensitized by ketones, have been provided with information indispensable for their full characterization, as nature of the excited state of the sensitizer (donor) from which energy is transferred, mechanism and kinetics of energy transfer, nature of the excited state of energy acceptor and products of photosensitized reactions. Triplet state is that state of excited ketones from which energy is most often transferred. It mainly occurs due to high efficiency of intersystem crossing and its longer life time than in the singlet state. It has been found lately, however, that the transfer of energy from ketones is also feasible from their excited singlet states⁷⁻¹¹⁾. As for photolysis of chlorobenzene sensitized by acetone¹²⁾ the results obtained hitherto do not allow to tell explicitly from what state of excited acetone the energy is transferred or what is the mechanism of the process. Considering this situation the investigations have been undertaken on the sensitizing effect of a number of other ketones in the photolysis of chlorobenzene and the more important of the preliminary results obtained have been presented in this note.

EXPERIMENTAL

Chlorobenzene p. (Zakł. Chem. Oświęcim) was desiccated over phosphorus pentoxide and distilled twice on 10-plate Brunn's column type. Acetone and 2-butanone a.p. (Merck Darmstadt) was desiccated over anhydrous potassium carbonate and magnesium sulfate and distilled on 1-metre column of Vigreux type. The same purifying procedure was applied to other ketones employed in the course of investigations: 2-pentanone p. (U.C.B. Belgium), 2-hexanone p. (Fluka Switzerland), 3-pentanone p. (U.C.B. Belgium) and cyclohexanone p. (Zakł. Chem. Oświęcim). Benzophenone p. (Polfa Kraków) was purified by recrystallization from ethanol and fluorenone p. (Schuchardt Munich) by recrystallization from a mixture of 1 volume of benzene and 2 volumes of petroleum ether. Cyclohexane a.p. (Zakł. Chem. Tarnów) used as solvent was desiccated over potassium hydroxide and distilled twice on 1-metre column of Vigreux type. The purity degree of the above mentioned reagents was tested by gas chromatography and spectral absorption analysis in ultraviolet.

The solutions studied were exposed to radiation of $\lambda \geq 300$ nm wavelength from a high pressure mercury lamp type TQ 150 (Original Hanau) which has been passed through a Pyrex filter 3 mm thick. A special reactor of Pyrex glass (Fig. 1) was used for this purpose, placed in a water thermostat at 293 ± 0.1 K. Concentrations of ketones employed in cyclohexane, except for benzophenone and fluorenone were successively: 1, 2, 3, 4 and 5 mole·dm⁻³ at constant chlorobenzene concentration 0.5 mole·dm⁻³. Prior to irradiation the solutions were washed with pure nitrogen previously passed through a washer with a solution of the same concentration as that prepared for irradiation reactor. The layer of the solution irradiated was 2 mm

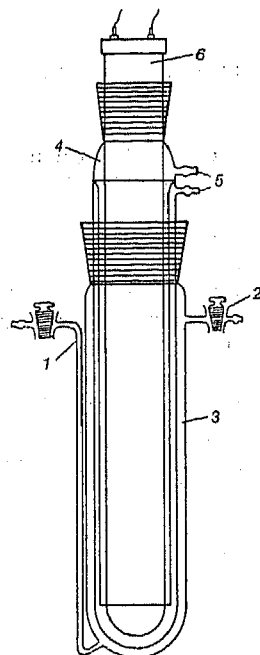


Fig. 1. 1 — inlet of nitrogen, 2 — outlet of nitrogen, 3 — irradiated solution, 4 — water jacket, 5 — inlet and outlet of water, 6 — TQ 150 lamp

thick. Hydrogen chloride evolving during the sensitized photolysis of chlorobenzene was washed out from cyclohexane solution with water distilled twice in a quartz apparatus and potentiometrically determined with a pH-meter type LBS-66 and 0.01 N AgNO₃. The error of precision of the determination did not exceed 5%. The times of irradiation of the solutions investigated changed by 2 to 8 hrs. Spectral curves of absorption of chlorobenzene solutions irradiated in presence and absence of ketones were taken by means of SP-700 Pye-Unicam spectrophotometer.

RESULTS AND DISCUSSION

Conversion degree of chlorobenzene to hydrogen chloride for different sensitizer concentrations in function of exposure time is presented in the Table. The data in the Table indicate that all the ketones used, except benzophenone and fluorenone, photosensitized the decomposition of chlorobenzene with different efficiency.

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Table
Degree of conversion of chlorobenzene to hydrogen chloride (%)

Sensitizer	Irradiation time (hrs)	Concentration of sensitizer (mole · dm ⁻³)				
		1	2	3	4	5
Acetone	2	0.13	0.35	0.39	0.50	0.15
	4	0.25	0.54	0.63	0.67	0.43
	6	0.30	0.72	0.87	0.73	0.68
	8	0.37	0.94	1.05	0.86	0.80
2-Butanone	2	0.20	0.40	0.40	1.00	2.30
	4	0.40	0.80	1.00	1.80	2.60
	6	0.40	1.60	1.20	2.20	2.70
	8	0.40	1.85	1.60	2.60	3.50
2-Pentanone	2	0.40	0.50	1.50	0.30	0.20
	4	0.80	0.80	1.70	0.40	0.40
	6	0.90	1.60	2.30	1.20	1.00
	8	1.15	1.80	2.40	1.60	1.50
3-Pentanone	2	1.05	1.20	1.20	1.70	1.10
	4	1.10	1.60	1.60	2.00	2.00
	6	1.30	2.40	2.60	2.40	2.40
	8	1.50	2.60	2.90	2.40	2.40
2-Hexanone	2	0.10	0.60	0.40	0.40	0.40
	4	0.15	0.80	0.45	0.45	0.45
	6	0.20	1.10	0.45	0.45	0.45
	8	0.25	2.20	0.45	0.45	0.45
Cyclohexanone	2	0.20	0.85	0.60	0.60	0.60
	4	0.75	1.00	0.70	1.20	1.20
	6	0.90	1.35	0.90	1.20	1.20
	8	1.20	1.80	1.50	1.20	1.20

In order to compare the photosensitizing properties, Fig. 2 shows how the relative conversion degree of chlorobenzene to hydrogen chloride (from now on referred to as RCD) depends on concentration of those ketones after 2 (A), 4 (B), 6 (C) and 8 (D) hours of exposure. Values of RCD were obtained from the degree of conversion after taking into account the differences in intensities of light ($\lambda = 313$ nm) absorbed by solutions of particular ketones in the reactor. Those differences decrease as the concentration of sensitizer in the solutions studied rises. The course of curves in Fig. 2 shows that ketones photosensitize the decomposition of chlorobenzene with various efficiency and more or less distinct maxima of RCD value are observed within the range of concentrations of exposure times used. 2-Butanone, 3-pentanone and 2-pentanone proved to be particularly efficient photosensitizers and the activity of ketones decreases in the following succession: cyclohexanone, 2-hexanone and acetone. Benzophenone within the concentration range from 1 to 3 mole · dm⁻³ and fluorenone at 0.5 mole · dm⁻³ used as photosensitizers proved to be nearly inactive. The

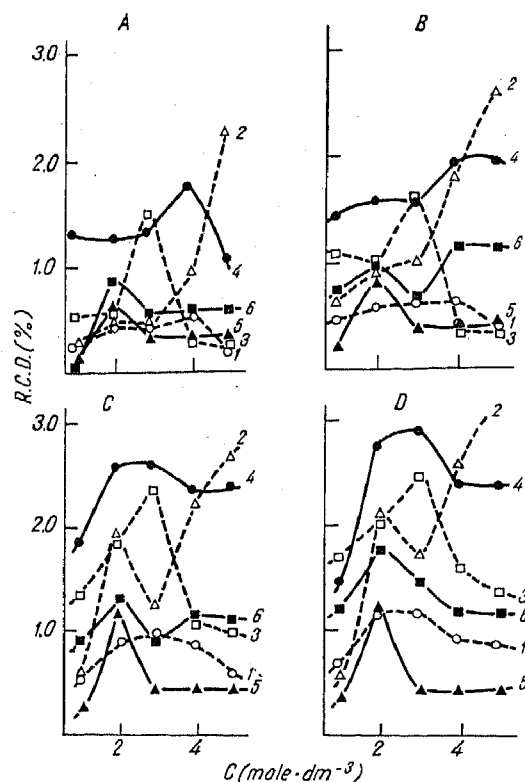


Fig. 2. The relative conversion degree of chlorobenzene to hydrogen chloride (RCD) as a function of sensitizer concentration after 2 (A), 4 (B), 6 (C), and 8 (D) hours of irradiation. Curves: 1—○—○—○—○—○—acetone, 2—△—△—△—△—2-butanone, 3—□—□—□—□—2-pentanone, 4—●—●—●—●—3-pentanone, 5—▲—▲—▲—▲—2-hexanone, 6—■—■—■—■—cyclohexanone

observed decrease in the RCD values (except 2-butanone) as the photosensitizer concentration rises is indicative of some competitive processes beginning to play an essential role in photosensitization at certain values of sensitizer concentration. They may be, for example, self-quenching or formation of excited dimers (excimer). It is a long time ago that Bowen and De La Praudiere¹³⁾ noticed the photoreactivity of pure liquid acetone to be considerably lower than that of its solutions, and Chapman and Wampfler¹⁴⁾, while studying dimerization of olefines photosensitized by some aromatic ketones, found that the efficiency of energy transfer from the excited triplet states of those ketones decreased as their concentrations rose to 1 mole·dm⁻³ but for such ketones as acetophenone and benzophenone it remained constant. Chambers et al.¹⁵⁾ have found, on the other hand, that the increased disappearance of uracyl dinucleotide due to dimerization of this compound occurs with a rise in concentration of acetone as photosensitizer in its concentration range from 0.034 to 0.21 mole·dm⁻³, which they accounted for by an increase in concentration of the excited donor molecules in triplet state. One of the important processes which must be taken into account in photosensitized reaction is the disappearance of excited molecules of the donor due to an interaction

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with its molecules in the ground state. A direct proof of such an interaction was supplied by Yang et al.¹⁰⁾ who have found that in a mixture of acetone-¹⁸O and acetone-d₆ occurs an isotope photochemical exchange of oxygen through the formation of dimers (1,3-dioxetanes) resulting in ordinary acetone and acetone-d₆-¹⁸O. So, the presence of maxima on the curve of RCD dependence on sensitizer concentration can be accounted for by the energy transfer as one of many possible processes of deactivating the excited molecules of the donor, and the efficiency of those processes is dependent on the sensitizer concentration and its physico-chemical properties, both in its excited and ground states. A rise in sensitizer concentration within the range of low concentrations increases, above all, the number of its excited molecules from which the energy can be transferred to the acceptor. A further increase in sensitizer concentrations affects less and less the rise in number of its excited molecules which, in turn, being among a larger number of molecules in the ground state, can interact with them at the expense of interactions with molecules of the acceptor, its concentration being, in this case, constant. At large concentrations of the sensitizer the appearance of the so-called back sensitization cannot be excluded; i.e. the transfer of energy from excited molecules of the acceptor to the molecules of the donor in the ground states. The sensitizer can also participate in secondary chemical reaction of products of the sensitized decomposition of the acceptor¹²⁾.

It is still to be explained from which state of excited ketone energy is transferred to chlorobenzene. Energy of the singlet state (S_1) estimated from absorption spectra $S_1 \leftarrow S_0$ for chlorobenzene is $427 \text{ kJ}\cdot\text{mole}^{-1}$ ($102 \text{ kcal}\cdot\text{mole}^{-1}$), and that of triplet state (T_1) obtained from absorption spectra $T_1 \leftarrow S_0$ for that compound is $341.6 \text{ kJ}\cdot\text{mole}^{-1}$ ($81.6 \text{ kcal}\cdot\text{mole}^{-1}$)¹⁷⁾. For acetone energy of excited singlet state (S_1) is $371.8 \text{ kJ}\cdot\text{mole}^{-1}$ ($88.8 \text{ kcal}\cdot\text{mole}^{-1}$), and that of triplet state (T_1) is $334.9 \text{ kJ}\cdot\text{mole}^{-1}$ ($80 \text{ kcal}\cdot\text{mole}^{-1}$)⁹⁾. For the other ketones employed in our investigations energy of excited singlet state (S_1) does not exceed that of excited singlet state (S_1) for acetone¹⁸⁾ so that of the triplet state (T_1) for those ketones may be expected not to exceed $334.9 \text{ kJ}\cdot\text{mole}^{-1}$ ($80 \text{ kcal}\cdot\text{mole}^{-1}$)¹⁹⁾. The energy value of C—Cl bond in chlorobenzene is ca. $360 \text{ kJ}\cdot\text{mole}^{-1}$ ($86 \text{ kcal}\cdot\text{mole}^{-1}$)²⁰⁾. Energy of excited singlet (S_1) and triplet (T_1) states of benzophenone and fluorenone is considerably lower than that of C—Cl bond in chlorobenzene and that is why those ketones are nearly inactive. The energy value of singlet state (S_1) of chlorobenzene is much higher than that of excited singlet state (S_1) of ketones (the energy difference amounts to about $54 \text{ kJ}\cdot\text{mole}^{-1}$ ($13 \text{ kcal}\cdot\text{mole}^{-1}$)), so the energy transfer process will be endothermic and, thus, not so likely to occur. The energy value of triplet state (T_1) of chlorobenzene is slightly higher than that of excited triplet state (T_1) of ketones (the energy difference amounts to about $6.7 \text{ kJ}\cdot\text{mole}^{-1}$ ($1.6 \text{ kcal}\cdot\text{mole}^{-1}$)) so the energy transfer process will be less endothermic and, thus, more likely to occur. It is also possible that the process of energy transfer will occur by collisional deactivation or formation of "exciplex" between excited molecule of ketone and molecule of chlorobenzene. Further investigations on energy transfer mechanism are being carried on and will be the object of another report.

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