less than 0.1 for the organic solvent. Tommila[4,6] has ascribed the increase in rate to the existence of both hydrophilic and hydrophobic groups in the activated complex. Because of the specific attractions of these groups, solvation of the complex should be greater in some mixtures of water and organic solvents than in water alone. The effects found for dioxane and acetone in binary mixtures with water were remarkable for their near equality,[4] and our results show that in the ternary solvent system dioxane–acetone–water these effects augment each other up to a mole fraction of acetone higher than 0.2.

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Photochemical Decomposition of Cyclohexanone, Cyclopentanone and Cyclobutanone[1]

BY F. E. BLACET AND ARNOLD MILLER

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Quantum yields of the photodecomposition products of these cycloketones have been determined in the ranges 3130–2537 Å. and 100–300°. Cyclohexanone principal products were carbon monoxide, cyclopentane and pentene-1; minor products were ethylene and propylene. At 2537 and 2654 Å. quantum yields were temperature independent. At 3130 Å. the yields of carbon monoxide, cyclopentane and pentene-1 increased with temperature. Cyclopentanone products were carbon monoxide, cyclobutane and ethylene. The yields were temperature dependent at 3130 Å., but independent at 2654 and 2537. Cyclobutanone products were carbon monoxide, cyclopropane, ethylene, propylene and presumably ketene. Yields were temperature independent at 3130 and 2654 Å. All the ketones gave some evidence of polymer formation and a polymerization quantum yield is given based on material balance. A general mechanism of photodecomposition has been proposed involving two primary chemical reactions, which accounts moderately well for all experimental results.

The photochemistry of cyclic ketones was initially investigated by Norrish and co-workers[2,3] and later by Benson and Kistiakowsky,[4] utilizing full radiation from mercury arcs. In this paper are given quantum yields obtained under controlled conditions of wave length and temperature for the vapor phase photolyses of cyclohexanone, cyclopentanone and cyclobutanone. Dunn and Kutschke[5] have published a few results obtained with cyclohexanone since the information given herein was reported originally.[1]

Experimental

Photolyses were performed in a 20-cm. cylindrical fused silica cell of 3 cm. diameter which could be maintained at desired temperatures. Monochromatic radiant energy obtained by the use of a quartz monochromator was measured with the aid of a phototube which had been calibrated at each wave length involved with a thermopile-galvanometer system. Photolysis products were identified and quantitatively analyzed by means of both mass spectrometric and microgas analytical techniques.

The cyclohexanone and cyclopentanone were prepared by drying and fractionating standard Eastman White Label material. Both the boiling points and refractive indices of the final products checked published values. Cyclobutanone was synthesized by the method of Roberts and Sauer.[6] The boiling point was 98.2° at 755 mm. and $n^{25}\mathrm{D}$ was 1.4191. These values are to be compared to 98–100° and $n^{25}\mathrm{D}$ 1.4189 reported by Roberts.

Absorption spectra of the three compounds determined in heptane solution, and determined also in the vapor phase for cyclohexanone and cyclopentanone, were in agreement with those reported previously.[4] The electronic absorption region of interest extends approximately from 2400 to 3400 Å. Cyclobutanone and cyclopentanone have several prominent absorption bands in this region, while the cyclohexanone spectrum has only a faint indication of structure.

TABLE I

QUANTUM YIELDS OF PRODUCTS IN THE PHOTOLYSIS OF CYCLOHEXANONE, CYCLOPENTANONE AND CYCLOBUTANONE

Cyclohexanone

Wave length, Å. Temp., °C.	3130 125	3130 300	2654 100–300	2537 100–300
$\Phi_{\text{carbon monoxide}}$	0.22	0.91	0.78	0.81
Φ_{ethylene}	.02	.02	.02	.03
$\Phi_{\text{propylene}}$	.03	.03	.02	.02
$\Phi_{\text{cyclopentane}}$	.06	.31	.28	.21
$\Phi_{\text{pentene-1}}$	.12	.59	.45	.32
$\Phi_{\text{polymerization}}$	.01	− .02	.03	.25

Cyclopentanone

Wave length, Å. Temp., °C.	3130 125	3130 225	2654 100–300	2537 100–300
$\Phi_{\text{carbon monoxide}}$	0.33	0.42	0.61	0.74
Φ_{ethylene}	.15	.34	.25	.21
$\Phi_{\text{cyclobutane}}$	.26	.17	.27	.21
$\Phi_{\text{polymerization}}$	.01	.10	.21	.43

Cyclobutanone

Wave length, Å. Temp., °C.	3130 100–300	3130[a] 100	2654 100–300
$\Phi_{\text{carbon monoxide}}$	0.35	0.40	0.53
Φ_{ethylene}	.51	.54	.53
$\Phi_{\text{cyclopropane}}$	.13	.14	.17
$\Phi_{\text{propylene}}$	.014	.014	.12
$\Phi_{\text{polymerization}}$	.21	.25	.24

[a] 70 mm. H_2O vapor and 136 mm. cyclobutanone in reaction cell.

Quantum yields obtained in the study of all three of the ketones are given in Table I. All values are averages based on duplicate runs at each temperature, except for one experiment shown for cyclobutanone in which water vapor was added to the reaction system. Mean deviations of quantum yields were from 4 to 7%. Exposure times averaged between three and four hours and at the several wave lengths absorbed intensity, I_a, varied between 1×10^{-8} and 1×10^{-9} Ein./l./sec. Where temperature ranges are indicated, quantum yields were found to be constant for runs

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Chicago meeting of the American Chemical Society, September, 1953.

[2] M. Saltmarsh and R. G. W. Norrish, *J. Chem. Soc.*, 455 (1935).

[3] C. H. Bamford and R. G. W. Norrish, *ibid.*, 1421 (1938).

[4] S. W. Benson and G. B. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

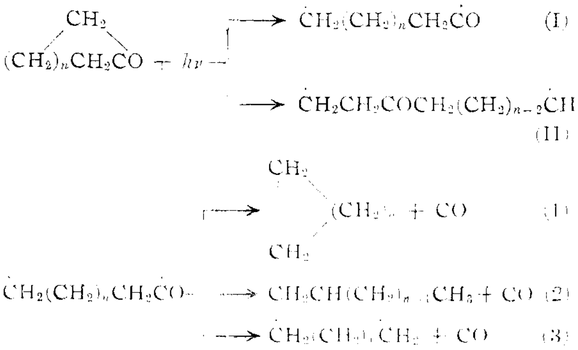
[5] J. R. Dunn and K. O. Kutschke, *Can. J. Chem.*, **32**, 725 (1954).

[6] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

made at seventy-five degree intervals within the range. Pressures of the ketones in all runs were between 100 and 150 mm., measured at 125°. "$\Phi_{\text{polymerization}}$," in the table, is a function postulated to attain material balance and is considered to be a measure of polymer formation, giving rise to an equivalent amount of carbon monoxide without production of like amounts of low molecular weight hydrocarbons. A light yellow non-volatile residue became evident in the reaction cell after several runs, especially at the shorter wave lengths. Mass spectra of butanone photolysis products contained prominent 42 and 41 peaks which were attributed to ketene. Because of experimental difficulties, no other direct evidence was obtained for this compound.

Discussion

Often temperature independence of quantum yields signifies intramolecular rearrangement in the primary process followed by unimolecular dissociation. Free radical primary processes, on the other hand, often lead to quantum yields which are temperature dependent since secondary reactions involving a radical and a normal molecule may occur requiring an activation energy of several kilocalories per mole. In this study, each ketone, at two different wave lengths, gave quantum yields which are temperature independent over a two-hundred-degree range, thus indicating non-free radical primary processes. Opposed to this concept, cyclohexanone and cyclopentanone show temperature dependence at 3130 Å. and all the ketones gave some polymerization under all experimental conditions. These facts perhaps can best be explained by postulating as primary photochemical processes the formation of biradicals by opening the rings followed for the most part by rapid dissociation of these radicals in a variety of ways to give stable molecules. The general mechanisms may be the following in which, however, reactions 4, 5 and 6 deal with biradicals from specific ketones.



$$\begin{matrix} CH_2 \\ (CH_2)_nCH_2CO \end{matrix} + h\nu \longrightarrow \dot{C}H_2(CH_2)_nCH_2\dot{C}O \qquad (I)$$

$$\longrightarrow \dot{C}H_2CH_2COCH_2(CH_2)_{n-2}\dot{C}H_2 \qquad (II)$$

$$\longrightarrow \begin{matrix} CH_2 \\ (CH_2)_n \\ CH_2 \end{matrix} + CO \qquad (1)$$

$$\dot{C}H_2(CH_2)_nCH_2\dot{C}O \longrightarrow CH_2CH(CH_2)_{n-1}CH_3 + CO \qquad (2)$$

$$\longrightarrow \dot{C}H_2(CH_2)_n\dot{C}H_2 + CO \qquad (3)$$

$$\dot{C}H_2CH_2CO(CH_2)_2\dot{C}H_2 \longrightarrow CH_2CH_2 + CH_2CHCH_3 + CO \qquad (4)$$

$$\dot{C}H_2CH_2COCH_2\dot{C}H_2 \longrightarrow CH_2CH_2 + CH_2CH_2 + CO \qquad (5)$$

$$\dot{C}H_2CH_2CO\dot{C}H_2 \longrightarrow CH_2CH_2 + CH_2CO \qquad (6)$$

$$X\ \dot{C}H_2(CH_2)_n\dot{C}H_2 + Y\ C_nH_{2n} \longrightarrow \text{polymers} \qquad (7)$$

The experimental evidence leaves doubtful the number of primary processes. However, *a priori* reasoning has led the authors to postulate two which lead to chemical change: reaction I, in which an α-carbon is separated from the carbonyl carbon, and reaction II, in which the energy absorbed in the carbonyl group is perhaps transmitted both ways around the ring causing rupture at or near the opposite side. (I) is the logical precursor of reactions 1, 2 and 3 and (II) of (4), (5) or (6), depending on the particular ketone under investigation. In considering the mechanics of the processes, it is reasonable to assume the initial breaking of a single carbon–carbon bond followed by other reactions of the resulting biradicals. The constant ratios of (1) and (2), and presumably (3), over a wide temperature range indicates that the biradicals first produced in (I) rapidly rearrange and dissociate without environmental influence. Since only photons of equal energy were used in a given experiment, this implies that the state of a ketone molecule at the moment of light absorption determined which of the three secondary adjustments would take place. Why this should be is not evident. It is not clear, also, why the ratios of (I) and (II) for all three compounds remain constant, as determined by the quantum yields of the products, at each of two wave lengths over a two-hundred-degree temperature range.

Cyclohexanone.—It follows from the assumed mechanism that Φ_{CO} is a measure of the sum of primary quantum yields, ϕ_{I} and ϕ_{II}. Reaction (II) is followed by (4), perhaps so inevitably that they could be combined in one concerted process. Thus, the quantum yields of ethylene or propylene, which are equal under all conditions employed, are a measure of ϕ_{II}. Since ϕ_{II}, thus estimated, was always small, Φ_{CO} is an approximate measure of ϕ_{I}. At wave lengths 2537 and 2654 Å. this indicates about 20% of the absorbed energy was dispersed by photophysical means, *i.e.*, by fluorescence or by thermal deactivation, independent of temperature over the range 100–300°. At λ 3130 Å., however, ϕ_{I} increases from about 0.2 to 0.9 over the range 125–300°, indicating that at this wave length the quantum energy is near, and perhaps slightly less than the activation energy which is necessary to rupture the molecules by (I).

At λ 3130 and λ 2654, the sum of quantum yields of pentene-1, cyclopentane and ethylene (or propylene) is equal to Φ_{CO}. This is not so at λ 2537 and $\Phi_{\text{polymerization}}$, involving reactions 3 and 7, was devised to account for the difference. In reaction 7, C_nH_{2n} may represent other biradicals or, as photolysis proceeded, the olefin products also may have become involved. Perhaps the marked decrease in quantum yield of pentene-1 found at λ 2537 from that obtained at λ 2654 can be accounted for in this way.

Cyclopentanone.—For this compound also, Φ_{CO} is a measure of the sum of ϕ_{I} and ϕ_{II}, and the values indicate that from one-fourth to two-thirds of the absorbed energy was dissipated photophysically, depending on experimental conditions. Reaction (II) presumably was followed always by (5), thus $^1/_2\ \Phi_{\text{ethylene}}$ equalled ϕ_{II}. The absence of a butene among the reaction products shows that under no condition employed did reaction (2) occur and, therefore, from the mechanism, (I) could be followed only by (1) and (3). At λ 3130 and 125°, $^1/_2\ \Phi_{\text{ethylene}}$ plus $\Phi_{\text{cyclobutane}}$ equals Φ_{CO}, indicating that (3) was not occurring, and therefore $\Phi_{\text{cyclobutane}}$ was a measure of ϕ_{I}. At 225° and this wave length and at both λ 2654 and 2537 over the temperature range studied, this simple relationship no longer held, indicating that reaction 3, followed by (7), was taking place. The absence of butene among the photolysis products may be interpreted to mean that the free radical cyclization reaction has a substantially lower activation energy than the reaction involving a hydrogen shift to form an olefin. This is to be expected since considerable strain would be present in the transition state required to form butene.

Cyclobutanone.—The large amount of ethylene formed from cyclobutanone indicates that reaction 6, involving the production of ketene, is important. Because ethylene was produced in excess of carbon monoxide at λ 3130, it was suggested originally that ketene further decomposed. To evaluate this hypothesis, water vapor was added in one instance on the assumption that it would react with the ketene vapor to form acetic acid. Experimental difficulties left the test for acetic acid in doubt and it may or may not have been produced. However, it is apparent from the results given in Table I that the water had no important effect on quantum yields and it follows, also, that it did not trap the postulated biradicals. In view of the results later obtained at λ 2654, appreciable ketene decomposition does not appear to have occurred in any event.

The general mechanism postulated above applies to this cycloketone, also. Accepting this mechanism, Φ_{CO} is a measure of ϕ_I and Φ_{ethylene} is a measure of ϕ_{II}. ϕ_I plus ϕ_{II}, estimated in this way, is about 0.9 at λ 3130 and 1, within experimental errors, at λ 2654; thus, for this compound, photochemical conversion of absorbed energy is high. Polymerization, reaction 7, was important under all conditions in which this ketone was studied.

LOS ANGELES, CAL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Thiourea Derivatives. III. Trimethylthiourea and Tetramethylthiourea

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

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Trimethylthiourea has been studied kinetically in aqueous solutions at elevated temperatures. This substance decomposes to form methylamine, dimethylamine and carbon oxysulfide as ultimate products in acid solutions. The decomposition is first-order and is uninfluenced by ionic strength in media of low *p*H. Rate constants at various temperatures and Arrhenius parameters are reported. Tetramethylthiourea also has been studied under similar conditions. This substance shows little or no tendency to react in neutral solutions. In acidic or basic media, however, hydrolysis is observed. The significance of these findings and their relevance to previous work is discussed.

Introduction

Thiourea,[1] methylthiourea[2] and the dimethylthioureas[3] have been studied previously in this Laboratory. Although some information on the chemistry of trimethylthiourea[4] and tetramethylthiourea[5] is available, no kinetic investigations with these compounds have been reported. The present work was, consequently, undertaken to secure rate data for these substances and to complete, thereby, our kinetic study of the methylated thioureas.

Experimental

Trimethylthiourea (1,1,3-trimethyl-2-thiourea) was prepared by the addition of dimethylamine to methyl isothiocyanate.[6] It was crystallized, m.p. 87° (lit.[4] 87°) twice from water solutions.

Anal. Calcd. for $C_4H_{10}N_2S$: C, 40.68; H, 8.54; N, 23.70. Found: C, 40.77; H, 8.50; N, 23.74.

Tetramethylthiourea (1,1,3,3-tetramethyl-2-thiourea) was prepared by heating bis-(dimethylthiocarbamyl) sulfide under air reflux for several hours,[7] followed by twice crystallizing the resulting mass from water. The product was then distilled at atmospheric pressure, b.p. 243° (lit.[8] 245°). Recrystallization from water gave the final product, m.p. 78° (lit.[8] 78°).

Anal. Calcd. for $C_5H_{12}N_2S$: C, 45.45; H, 9.14; N, 21.1. Found: C, 44.94; H, 8.68; N, 19.6.

The analytical methods for thiocyanate, ammonia, methylamine and dimethylamine have been described.[1-3] Total amine produced was also determined according to the following procedure. Reaction solutions of the thiourea under study were made 10 to 20 m*M* in standard acid, and the samples were then allowed to react until the total amine concentration was approximately 4 m*M*. The unreacted acid in the samples was subsequently determined by titration with standard NaOH (approximately 10 m*M*). During the titration the *p*H was read at convenient intervals and the end-point taken as the point when the change of *p*H with a small increment of standard basic solution was a maximum. Titration blanks were always run on aliquots of the unreacted experimental solutions. Results given by this method were compared with those obtained by our usual spectrophotometric techniques. Within the combined experimental uncertainties, the two methods gave identical results.

The procedures used in conducting the kinetic runs and the apparatus employed in this investigation have been described in previous work.[1-3]

Results

Reacted solutions of trimethylthiourea were found to contain methylamine, dimethylamine and carbon oxysulfide. The rates of formation of methylamine and dimethylamine were followed and the corresponding empirical first-order rate constants, k_3 and k_4, were calculated by the rate equation previously presented. Measurements were made with 0.015 *M* H_2SO_4 and 0.015 *M* HNO_3 solutions. These solutions also contained tri-

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