It might be expected that the electron-donating effect of the primary amino group would be greater than the tertiary amino group, because the former would be converted to a salt ($-NH^-Li^+$ or $-N^{--}2Li^+$), by the reagent; this effect is probably more than compensated for by the insolubility of the lithium salts in the reaction medium.

Experimental[5]

General Procedure.—The reactions were carried out in solvents dried over sodium; the lithium aluminum hydride was used in about 1.0 m. solution in diethyl ether, the concentration of which was determined by titration.[6]

For each mole of a compound being reduced the stoichiometric amount of lithium aluminum hydride was taken as that required for reaction with all the active hydrogens in the molecule, plus one equivalent more than that needed to reduce the oxygen function to a carbinol. (For example, one mole of *p*-aminobenzophenone required two equivalents (one-half mole) of lithium aluminum hydride for reaction with the amino hydrogens, one equivalent for reduction of the ketone to a carbinol, and an additional equivalent for hydrogenolysis to the diphenylmethane.)

The equivalents employed in excess of this amount are recorded in the table.

The solid products were purified by crystallization, occasionally with a preliminary extraction with ligroin to separate the product from gummy residues. The products were identified as suitable solid derivatives, which had the expected m. p.'s; in several cases, mixed m. p.'s were taken with known samples. Some of the details about identification of the products are omitted, as the compounds are well known.

Isolation Procedures (A).—To the reaction mixture was added sufficient water-saturated diethyl ether to decompose the excess lithium aluminum hydride and hydrolyze the addition complex. At least twenty-four hours were allowed for the hydrolysis to be completed. The inorganic precipitate was then filtered off, washed with ethanol and (1) discarded or (2) treated further to remove adsorbed organic material. The filtered solvent solution and ethanol washings were combined.

(B) To the reaction mixture was added (1) 10% sulfuric acid (200 cc.) or (2) 10% sodium hydroxide (200 cc.) or (3), saturated Rochelle salts (200 cc.) and 10 cc. of 5% sodium hydroxide. After hydrolysis the solvent layer was separated and the aqueous layer extracted with five 200-cc. portions of diethyl ether. The aqueous residue from the extractions was (a) discarded or (b) continuously extracted for twenty-four to forty-eight hours to obtain additional organic product.

The combined solutions from (A) or the combined extracts from (B) were dried over Drierite and the solvents removed, usually under reduced pressure.

Summary

Aromatic acids, esters, aldehydes and ketones, with an amino group ortho or para to the oxygen function, have been found to undergo hydrogenolysis by excess lithium aluminum hydride, with conversion of the oxygen function to a methyl, or methylene group, in the case of ketones. The reaction apparently goes through the intermediate formation of the benzyl alcohol, which has been shown to undergo hydrogenolysis to a methyl group. The mechanism of the reaction has been discussed.

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[5] Melting points are corrected; boiling points uncorrected.

[6] Krynitsky, Johnson and Carhart, *Anal. Chem.*, **20**, 311 (1948).

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER, N. Y., AND THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY, CHICAGO, ILL.]

The Reaction of Cyclopentane with Mercury 6($^3P_1$) Atoms[1]

BY G. A. ALLEN,[2] D. L. KANTRO AND H. E. GUNNING

Investigation by Gunning and Steacie[3] of the reaction of cyclopropane with mercury 6($^3P_1$) atoms at 30.0° indicates that this reaction proceeds mainly through the initial formation of the trimethylene biradical by direct scission of a C–C bond. This differs markedly from the behavior of the paraffins,[4-8] which appear to react with mercury 6($^3P_1$) atoms at room temperature by the initial splitting of a C–H bond. Furthermore, cyclopropane contrasts strongly with the olefins[9-14] and diolefins,[11,15] whose reactions seem to proceed at the same temperature mainly by an excited molecule mechanism.

Accordingly, it was thought of interest to investigate the reaction of cyclopentane with mercury 6($^3P_1$) atoms in a static system at 30.0°, with a view to discovering whether its initial quenching process would resemble that of cyclopropane, the paraffins, or the olefins.

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[2] Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

[3] H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **17**, 351 (1949).

[4] K. Morikawa, W. S. Benedict and H. S. Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

[5] (a) E. W. R. Steacie and R. L. Cunningham, *ibid.*, **8**, 800 (1940); (b) B. de B. Darwent and E. W. R. Steacie, *ibid.*, **16**, 381 (1948); (c) E. W. R. Steacie and D. J. Dewar, *ibid.*, **8**, 571 (1940).

[6] B. de B. Darwent and E. W. R. Steacie, *ibid.*, **13**, 563 (1945).

[7] A. W. Hay and C. A. Winkler, *Can. J. Research*, **B21**, 149 (1943).

[8] B. de B. Darwent and C. A. Winkler, *J. Phys. Chem.*, **49**, 150 (1945).

[9] D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.*, **9**, 829 (1941).

[10] D. J. LeRoy and E. W. R. Steacie, *ibid.*, **10**, 676 (1942).

[11] H. E. Gunning and E. W. R. Steacie, *ibid.*, **14**, 57 (1946).

[12] H. E. Gunning and E. W. R. Steacie, *ibid.*, **16**, 926 (1948).

[13] H. E. Gunning and E. W. R. Steacie, *ibid.*, **14**, 581 (1946).

[14] G. A. Allen and H. E. Gunning, *ibid.*, **16**, 1146 (1948).

[15] H. E. Gunning and E. W. R. Steacie, *ibid.*, **12**, 484 (1944).

Experimental

For a description of the static reaction system and experimental technique used, reference should be made to the paper of Allen and Gunning on the mercury photosensitized reactions of isobutene.[14] In the current work, however, it should be noted that Cenco "Sealstix" was used to seal the ground glass joint connecting the reaction cell to the reaction system.

The cyclopentane used in this investigation was obtained in 5 ml. ampoules from the National Bureau of Standards (Standard Sample No. 219-5s; stated impurities 0.05 ± 0.02 mole per cent.). The ampoule to be used, equipped with an internal break-off tip and an iron-in-glass hammer, was attached to the section of the system adjoining the reaction cell through a Warrick–Fugassi type valve.[16]

Hydrogen used in the work was obtained from the Ohio Chemical and Manufacturing Company, Cleveland, Ohio (minimum purity 99.9%). It was passed into the evacuated system through two traps immersed in liquid nitrogen to remove any water, carbon dioxide or other condensable impurity, and was then stored without further purification in a two-liter flask provided with another Warrick–Fugassi valve.[16]

The mercury resonance lamp was operated at 20 milliamperes lamp current, corresponding to 29 volts input to the transformer. A sulfidized copper gauze, placed between the lamp and the cell, further reduced the incident intensity to a value which permitted accurate determination of the pressure changes in the system by means of an automatic Pearson differential manometer.[17]

One single-pass run was made, using apparatus similar to that described for the single-pass runs made on isobutene.[14] The hydrogen formed during this run was continuously removed by means of the Toepler pump in the analytical section of the system, and was measured in the gas buret at the conclusion of the run.

An analytical section, consisting of two fractionation traps, a mercury vapor diffusion pump with McLeod gage, a Toepler pump, a gas buret with capillary manometer, and a hydrogen combustion unit, was connected to the reaction system through a cut-off. The combustion unit consisted of a small trap containing cupric oxide deposited on glass wool, together with two other traps which permitted the freezing out of water formed in the combustion; a Warrick–Fugassi type valve[16] connected the gas buret to the combustion unit, while a cut-off made the return connection from the unit to the low-pressure side of the diffusion pump. Other cut-offs permitted the separation of the first fractionation trap from the second, and of the second from the diffusion pump. All cut-offs utilized mercury, with glass check-valves.

At the conclusion of each run, the residual cyclopentane and other condensables were frozen out in a small finger trap adjacent to the reaction cell. The non-condensable products were then pumped into the gas buret of the analytical section, first passing through the fractionation traps, one of which was immersed in liquid nitrogen to ensure removal of all condensable material. After the non-condensables were measured in the gas buret, the hydrogen present was burned in the combustion unit, and the residual gas was then returned to the gas buret for measurement.

The condensable portion of the reaction mixture of each of several runs was fractionated in the fractionation traps; thd entire condensable portion or any isolated fraction could be removed from the system by freezing it over into a 3-mm. o. d. sample tube immersed in liquid nitrogen and sealing the tube with the torch.

A partial fractionation of the products of the single-pass run was carried out, and the residual fraction removed from the system in the manner described. Through the kindness of the Eastman Kodak Company and Mr. G. P. Happ of their Research Laboratories, this fraction and the condensable portions of the reaction mixtures from runs A-8 and A-26, together with samples of cyclopentane and cyclopentene, were run on a mass spectrometer.

The high-boiling fractions isolated from two runs (A-48 and A-49) were sent to Clark Microanalytical Laboratory, Urbana, Illinois, for carbon–hydrogen analysis (by combustion), molecular weight determination by the Rast method, and a terminal methyl determination.

After runs A-40, A-41, A-42 and A-43, the cell was rinsed with *n*-hexane, the rinsings were combined, and the hexane was distilled off under vacuum. The containing vessel was then examined visually for evidence of polymer.

A further set of fifteen static runs (henceforth referred to as the "B" series), was made at an initial pressure of 200 mm. The total decomposition never exceeded 2% in these runs. The hydrogen was pumped off while the condensable products were frozen down in liquid nitrogen. The combined condensable products from the fifteen runs were then carefully fractionated, using suitable refrigerants, into a "C_5" fraction, and a high-boiling fraction. A mass spectrometric analysis of the "C_5" fraction was performed by Dr. Fred L. Mohler, Chief of the Mass Spectrometry Section of the National Bureau of Standards. The refractive index and the boiling point of the high-boiling fraction were determined. The micro boiling point determination used is described in Shriner and Fuson.[18] The boiling point values were corrected to 760 mm. by means of the formula

$$\Delta T = 1.2 \times 10^{-4}\, T_B \times \Delta P^{19}$$

These corrections never exceeded 0.7°K.

The intensity of the light incident upon the cell was determined by means of the uranyl oxalate–oxalic acid actinometer, as described in the authors' earlier paper.[14]

Results

Figure 1 shows a typical run at an initial pressure of 81 mm. of cyclopentane. As can be seen from the graph, the curve consists of three portions. There is a period of slight pressure rise AB, followed by a period BCD during which the pressure decreases at an increasing rate. This is followed by a linear portion DE; the slope of this line is taken as the rate of pressure decrease. (In the case of long runs, the linear portion was followed by a portion of decreasing rate of pressure

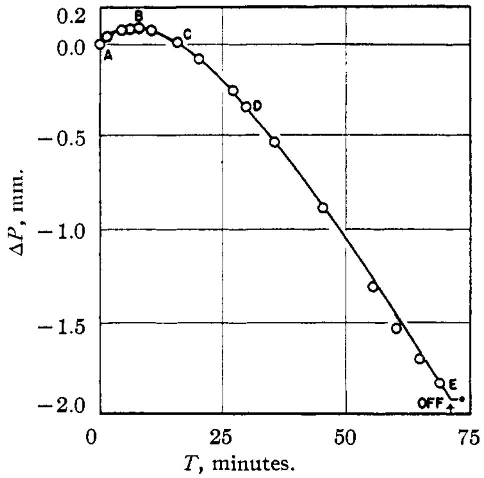

Fig. 1.—Pressure change, *vs.* time: run A-39; P_0 = 81 mm.

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[16] E. Warrick and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **15**, 13 (1943).

[17] D. J. LeRoy, *ibid.*, **17**, 652 (1945).

[18] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 93–94.

[19] MacDougall, "Thermodynamics and Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 122-123.

decrease; this may have been due to the accumulation of products, or to the decrease in concentration of initial reactant.) The time of the portion AC is approximately independent of initial pressure. Both the magnitude of the initial pressure rise and the initial rate of pressure rise increase somewhat with initial pressure, but neither could be measured with sufficient accuracy to permit any quantitative study to be made.

Table I

Rates of Pressure Decrease

Run	P_0, mm.	Duration, minutes	$-dP/dt$, moles/min. $\times 10^8$
A-38	5.0	60	14.1
A-37	12.5	70	22.2
A-25	35	90	43.3
A-29	35	90	39.1
A-30	35	90	38.2
A-19	50	90	50.1
A-39	81	70	63.6
A-52	114	90	68.4
A-36	116	90	69.9
A-50	195	255	103
A-41	199	255	104
A-40	199.5	255	109
A-48	200	255	102
A-42	201	255	107
A-44	202	255	160
A-49	202	255	102
A-43	205	255	107
A-31	211	90	116

The observed rates of pressure decrease, as defined above, are shown in Table I, and are plotted in Fig. 2 against the initial pressure of the cyclopentane. It is of interest to note that these rates increase with initial pressure throughout the entire pressure range investigated, although quenching should surely be complete for initial pressures above 20 or 30 mm., by analogy with cyclopropane.[1]

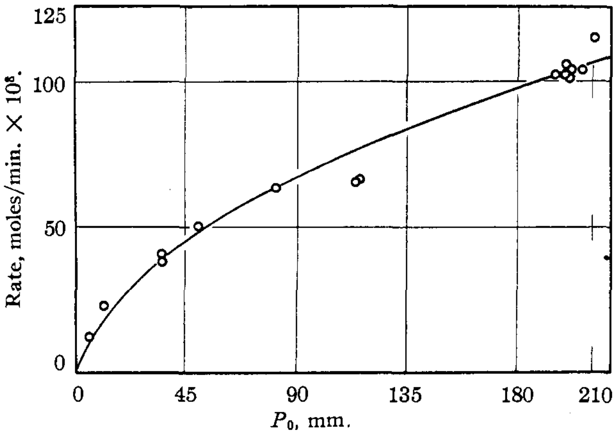

Fig. 2.—Rate of pressure decrease *vs.* initial pressure, P_0.

The non-condensable gas found among the products of the reaction was completely burned in the copper oxide combustion unit, thus establishing that it consisted entirely of hydrogen. The amount of hydrogen formed during runs of constant duration increased with increasing initial cyclopentane pressure, as is shown by the data of Table II; the same data show that for constant initial pressure, the average rate of hydrogen formation (*i. e.*, hydrogen formed during the run divided by the duration of the run) decreased with increasing duration of the run. Comparison of these average rates of hydrogen formation with the rates of pressure decrease for runs made at the same initial pressure shows that the rate of pressure decrease is much less than the corresponding average rate of hydrogen formation at low initial pressures, but approaches it as the initial pressure increases.

Table II

Hydrogen Formation as a Function of Initial Pressure and of Time

Run	Duration, minutes	Hydrogen formed, moles $\times 10^6$	Run	Duration, minutes	Hydrogen formed, moles $\times 10^6$
P_0 = 35 ± 0.5 mm.			P_0 = 51 ± 2 mm.		
A-24	3	3.51	A-21	3	3.49
A-27	5	5.08	A-17	5	5.73
A-8	20	18.2	A-18	15	14.3
A-25	90	62.7	A-11	25	23.0
A-29	90	58.7	A-7	25	23.0
A-30	90	60.3	A-12	25	22.4
P_0 = 81 ± 0.5 mm.			A-20	45	37.8
A-46	3	3.61	A-19	90	68.1
A-47	5	5.63	P_0 = 207 ± 4 mm.		
A-39	70	60.7	A-32	3	4.1
P_0 = 115 ± 1 mm.			A-33	5	6.98
A-34	3	3.84	A-14	25	29.2
A-35	5	6.12	A-31	90	90.1
A-10	25	26.8	A-43	255	214.6
A-36	90	76.7			

The mass spectra of the reaction mixtures from runs A-8 and A-26 showed a slight enhancement of the mass peak at 67 over that for pure cyclopentane, but no other difference could be detected. However, when the fraction of the single-pass run was run on the mass spectrograph at high pressure (0.30 mm.), mass peaks were detected at masses of 139 ± 1, 111 ± 1, and 110 ± 1. The high-boiling fraction of the long, high-pressure runs A-44 and A-48 to A-50 was a liquid having a very low vapor pressure at room temperature. Carbon-hydrogen analysis on this material from run A-48 showed C, 86.58; H, 13.25, while analysis of the material from run A-49 showed C, 87.07; H, 12.89. Molecular weight determination on the material from run A-48 gave results of 131 and 138. Theoretical results are: for $C_{10}H_{18}$, molecular weight, 138.1; C, 86.88; H, 13.13; for $C_{10}H_{16}$, molecular weight, 136.1; C, 88.17; H, 11.83. A terminal methyl determination by oxidation on the high-boiling fraction from the "A" series was negative.

Fractionation of the condensable portion of the reaction mixtures of several runs from the "A" series yielded no fraction below the residual cyclopentane one. These results would therefore indicate the absence of C_2 and C_3 compounds among the products of the reaction.

Distillation of the *n*-hexane solvent from the cell-rinsings of runs A-40 to A-43, inclusive, left a minute but observable trace of a non-volatile residue. The quantity observed was so small as to suggest that this polymer was a minor or secondary product of the reaction.

The mass spectrometric analysis of the "C_5" fraction from the "B" series of runs, which would also contain any condensable products of lower molecular weight, gave the result: cyclopentene, 0.2 mole per cent.; cyclopentane, 99.8 mole per cent. These results tend to confirm our previous statement that no hydrocarbons lower than "C_5" are present. The presence of cyclopentene is also confirmed. It might also be mentioned that the olefinic cyclopentene would not be expected to accumulate in the system since its quenching cross section would be large in comparison to cyclopentane. These conclusions are substantiated by the work of Gunning and Steacie[3] on the addition of small amounts of propylene to cyclopropane, under which conditions the quenching of the mercury $6(^3P_1)$ atoms is predominantly by propylene.

The refractive index of the high-boiling fraction from the "B" series was n_D 1.4639 ± 0.00004 at 20°. Recent values for n^{20}_D for cyclopentylcyclopentane in the literature vary from 1.4638[20] to 1.4641.[21]

The micro-boiling point determinations[18] on the high-boiling fraction, gave the value 189.3° at 748.2 mm., adjusted[19] to 190.0° at 760 mm. Literature values for the boiling point of cyclopentyl cyclopentane are 190.0° to 190.5° at 761.8 mm.,[21] and 189–191° at 760 mm.[20] It therefore appears to be quite justifiable to identify the high-boiling fraction with cyclopentylcyclopentane.

Runs carried out with a nine-fold excess of hydrogen added showed a marked decrease in the rates of pressure decrease as compared with the values observed for the same initial pressures of cyclopentane.

The average value of three determinations of light intensity was 2.4×10^{-6} einsteins/minute. This together with the data of Table II indicates that the initial quantum yield of hydrogen formation is about 0.5, increasing slightly with increasing initial pressure and decreasing with time during a given run.

Two runs, made to investigate the possible effects of intermittent irradiation, indicate the complete absence of intermittency effects both during the induction period (ABCD of Fig. 1) and during the period of linear pressure decrease (DE of Fig. 1).

Discussion

The main observations which must be explained by any mechanism proposed for the reactions of cyclopentane with mercury $6(^3P_1)$ atoms may be summarized as follows: (a) The pressure initially increases slightly, but begins to decrease after 8–10 minutes exposure; the rate of pressure decrease becomes independent of time after the first 25–30 minutes of exposure. (b) The rate of pressure decrease increases with increasing initial pressure of cyclopentane, even in the pressure region where it may be assumed that quenching is complete. (c) Hydrogen is a major product of the reaction. (d) The rate of hydrogen formation decreases with time of exposure. (e) The initial rate of hydrogen formation increases slowly with increasing initial pressure of cyclopentane. (f) At low initial cyclopentane pressures, the rate of hydrogen formation is greater than the rate of pressure decrease; as the initial pressure is increased, the rate of pressure decrease approaches that of hydrogen formation. (g) The only hydrocarbon products of the cyclopentane decomposition are cyclopentene and cyclopentylcyclopentane. (h) Very small amounts of a low-vapor-pressure hexane-soluble polymer are deposited on the cell walls during long, high-pressure runs. (i) The presence of added hydrogen in the initial reaction mixture decreases the rate of pressure decrease below the value observed for the same pressure of cyclopentane.

It is immediately apparent from (b) that no excited molecule mechanism need be postulated for this reaction. It is interesting to note that no excited molecule appears to be formed by cyclopropane[1] in its reactions with mercury $6(^3P_1)$ atoms; in fact, the rate of pressure decrease observed in this reaction is constant for pressures in the complete quenching region. Cyclohexane also appears to form no excited molecule in its analogous reactions, resembling cyclopentane in that the rate of pressure decrease increases with increasing initial pressure even in the complete quenching region.[22]

If the initial quenching process resulted in the direct formation of C_5H_8 and hydrogen, analogous to the ethylene[9,10] and butadiene[15] reactions, the pressure would increase with time during a run. A pressure decrease might occur as the result of secondary quenching by one or both products; but such quenching and hence such pressure decrease would become less important as the initial cyclopentane pressure increased. The reaction

$$\text{cyclo-}C_5H_{10} + Hg\ 6(^3P_1) \longrightarrow Hg\ 6(^1S_0) + \text{cyclo-}C_5H_8 + H_2 \quad (1)$$

hence cannot be considered as the major quenching step in this reaction.

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[20] E. B. Evans, *J. Inst. Petroleum Tech.*, **24**, 548 (1938).

[21] G. E. Goheen, THIS JOURNAL, **63**, 744 (1941).

[22] H. E. Gunning, unpublished data.

The only plausible manner in which the observed products can result in a sizeable pressure decrease is by condensation of the $C_{10}H_{18}$ product during the course of the run. That this does occur seems probable in view of the low vapor pressure observed, and appears almost certain when the failure of the liquid product formed in run A-53 to vaporize for run A-54 is considered.

The possibility of an initial carbon–carbon bond scission cannot be definitely excluded on the basis of the above data; however, the formation of hydrogen and $C_{10}H_{18}$ as major products does not seem capable of ready explanation by means of any mechanism involving the pentamethylene biradical. It is also extremely difficult to explain on this basis the observation that the rate of pressure decrease is less than the rate of hydrogen formation at low initial cyclopentane pressures.

A reasonable mechanism which is consistent with all the observed data can be set up on the basis of an initial splitting of a carbon–hydrogen bond in the cyclopentane molecule. Consider the sequence

$$\text{cyclo-}C_5H_{10} + \text{Hg } 6(^3P_1) \longrightarrow$$
$$\text{Hg } 6(^1S_0) + \text{cyclo-}C_5H_9 + H \quad (2)$$
$$H + \text{cyclo-}C_5H_9 \longrightarrow \text{cyclo-}C_5H_8 + H_2 \quad (3)$$
$$H + \text{cyclo-}C_5H_9 \longrightarrow \text{cyclo-}C_5H_{10} \quad (3a)$$
$$H + \text{cyclo-}C_5H_{10} \longrightarrow H_2 + \text{cyclo-}C_6H_9 \quad (4)$$
$$\text{cyclo-}C_5H_9 + \text{cyclo-}C_5H_9 \longrightarrow \text{cyclo-}C_{10}H_{18} \quad (5)$$

where the cyclopentylcyclopentane is assumed to attain its vapor pressure rather rapidly, after which time it condenses out in the cell as rapidly as it is formed.

It can be seen that this mechanism accounts for the three major products observed, namely, hydrogen, cyclopentene and cyclopentylcyclopentane. Furthermore, the time lag observed before the pressure decreases is accounted for by the necessity of building up the gas-phase $C_{10}H_{18}$ concentration to its vapor pressure before condensation commences. The initial pressure rise observed may be partly due to the same physical effects suggested to explain the initial pressure rise observed for the isobutene reaction[14]; in addition reaction (3) will be pressure-increasing, so that the over-all reaction prior to condensation of the $C_{10}H_{18}$ product will likewise be pressure-increasing.

While the assumption of steady-state concentrations of radicals does not permit the determination of the explicit kinetics predicted by the proposed mechanism, the implications can readily be noted. Thus, if the rate of reaction (2) is given, in the complete quenching region, by the expression KI_a, where K is a constant equal to or less than unity and I_a is the intensity of the absorbed light, then the rate of hydrogen formation is given by the expression

$$\mathrm{d}H_2/\mathrm{d}t = KI_a - k_{3a}[k_4(C)/k_5]^{1/2}(H)^{3/2}$$

where (C) is the concentration of cyclopentane. Similarly, the rates of formation of C_5H_8, of $C_{10}H_{18}$, and the rate of pressure decrease are given by the expressions

$$\mathrm{d}C_5H_8/\mathrm{d}t = k_3[k_4(C)/k_5]^{1/2}(H)^{3/2}$$
$$\mathrm{d}C_{10}H_{18}/\mathrm{d}t = k_4(H)(C)$$
$$= KI_a - (k_3 + k_{3a})[k_4(C)/k_5]^{1/2}(H)^{3/2}$$
$$-\mathrm{d}P/\mathrm{d}t = k_4(H)(C) - k_3[k_4(C)/k_5]^{1/2}(H)^{3/2}$$
$$= KI_a - (2k_3 + k_{3a})[k_4(C)/k_5]^{1/2}(H)^{3/2}$$

It should be remarked that the product $(H)^{3/2} \cdot (C)^{1/2}$ decreases with increasing initial cyclopentane pressure. For this reason, the rate of pressure decrease should approach the rate of hydrogen formation as the initial pressure is increased, in agreement with our data.

Since the quantum yield of hydrogen formation does not begin to approach unity at the highest pressures used, where the rate of pressure decrease approaches the rate of hydrogen formation, the inefficiency constant K must be less than unity, *i. e.*, the recombination step (3a) is not adequate to explain the fact that the quantum yield of hydrogen formation is about 0.5. However, it is necessary to include this step in the mechanism if the increase in rate of hydrogen formation with increase in initial pressure is to be explained.

The activation energies of the paraffinic analogs of reactions (3) and (4) are of the order of 5 to 8 kcal.[23]; hence, on the basis of these analogies, postulation of reactions (3), (3a) and (4) appears reasonable. Since the rate of pressure decrease increases more rapidly with increasing initial pressure than does the rate of hydrogen formation, k_3 must be greater than k_{3a}, and hence it must be concluded that on the basis of the proposed mechanism, the activation energy of reaction (3a) is either greater than that of reaction (3), or the steric factor for reaction (3a) is much less than that for reaction (3).

In the runs with a nine-fold excess of hydrogen added, the hydrogen should do the major part of the quenching; such quenching would result in the inefficient formation of hydrogen atoms,[24] which could then lead to a pressure decrease through reactions (4) and (5) followed by the condensation of the $C_{10}H_{18}$ product. The inefficiency of hydrogen atom formation by hydrogen quenching might well explain the decrease in rate of pressure decrease observed in these runs.

The decrease of rate of hydrogen formation with time may be due to the absorption of incident light by a thin layer of $C_{10}H_{18}$ condensed on the cell window, resulting in an effective change in the value of I_a. Alternatively, the reaction products may compete with the cyclopentane in the initial quenching step, though this effect would be expected to continue to increase with increasing time of exposure.

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[23] For reviews of the evidence for this statement, see W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corporation, New York, N. Y., 1941; also E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, Chapter VI.

[24] L. B. Thomas and W. D. Gwinn, THIS JOURNAL, **70**, 2643 (1948).

Energy considerations require that the C_5H_9 radical be cyclic, since the 112 kcal./mole available for reaction (2) is insufficient to open the cyclopentane ring simultaneously with the splitting off of a hydrogen atom—an additional confirmation of the identification of the $C_{10}H_{18}$ product with cyclopentylcyclopentane.

In view of the small quantity of polymer formed in the long exposure runs it is not necessary to account for its formation in the main mechanism; it seems probable that it is formed by secondary reactions of the products.

Conclusions

The reaction of Hg $6(^3P_1)$ atoms with cyclopentane bears great resemblance to the reactions of Hg $6(^3P_1)$ atoms with the lower paraffins[2-8,25] (with the exception of methane and neopentane). It differs markedly from those of the olefins which have been investigated to date in that cyclopentane shows no evidence of reacting *via* an excited molecule. Furthermore, the mercury photosensitized reaction of cyclopentane is shown to contrast strongly with the thermal reaction of cyclopentane, where the products are hydrogen and cyclopentadiene, or alternatively ethylene and propylene.

Further investigations of the mercury photosensitized reactions of cyclopentane and other cyclic paraffins are now in progress in the laboratories of one of us (H. E. G.).

Acknowledgment.—It is a sincere pleasure for the authors to acknowledge their indebtedness to Mr. G. P. Happ and the Eastman Kodak Company and to Drs. Fred L. Mohler and Vernon H. Dibeler of the National Bureau of Standards for performing a number of very helpful mass spectrometric analyses in connection with this investigation.

Summary

An investigation has been made of the reaction of cyclopentane with mercury $6(^3P_1)$ atoms in a static system at 30°, over the pressure range from 5–200 mm.

The products of the reaction are hydrogen, cyclopentene and cyclopentylcyclopentane.

The linear pressure decrease observed is attributed to the condensation of the cyclopentylcyclopentane.

Both the nature of the products formed and the quantum yield suggest that the mercury photosensitized decomposition of cyclopentane strongly resembles those of the lower paraffins.

A mechanism is proposed, involving the formation of cyclopentyl radicals, which is consistent with the data observed.

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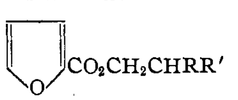
[25] B. de B. Darwent and E. W. R. Steacie, unpublished data.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

The Preparation of Some *exo*-Nitro Derivatives of Substituted 5-Nitrofurans[1,2]

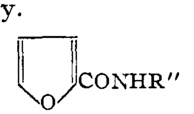
BY HENRY GILMAN AND HARRY L. YALE

The preparation of several new *exo*-nitro-5-nitrofurans was undertaken in order to evaluate them as explosives. Three types of furan compounds were utilized in this study.



R or R′ = H, OH, CH_2Cl or CH_3

I



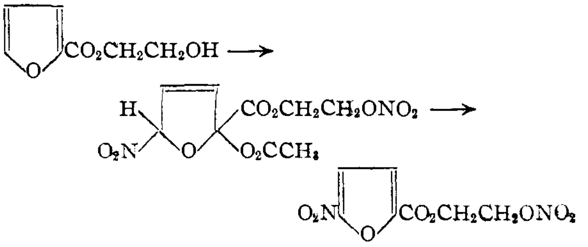
R″ = H or alkyl

II

R‴ = H or alkyl

III

The esters represented by Type I were prepared by the reaction between furoic acid and ethylene oxide, epichlorohydrin or propylene oxide in the presence of catalytic amounts of anhydrous ferric chloride. Nitration of these esters by means of nitric acid (d. 1.5) in acetic anhydride proceeded smoothly through the intermediate nitro compound[3] which, after treatment with pyridine, gave the desired *exo*-nitro-5-nitrofuran compound.



The amides represented by Type II were best prepared by the reaction of the acid chloride and the amine or ammonia. When N-methyl-5-nitrofuramide was treated with distilled white fuming nitric acid at 0° there was obtained a 65.3% yield of N-methyl-N,5-dinitrofuramide.

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[1] The work reported here was done under the auspices of a contract between O. S. R. D. and Iowa State College.

[2] Drs. Crane and Capell of *Chemical Abstracts* have suggested the nomenclature used in this paper.

[3] Freure and Johnson, THIS JOURNAL, **53**, 1142 (1931). The most recent paper on the structure of the intermediate nitration product of furan is by Clauson-Kaas and Fakstorp, *Acta Chem. Scand.*, **1**, 210 (1947).