[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF UTAH]

Formation of Ketene in the Photolysis of Acetone[1]

BY ROBERT C. FERRIS[2] AND W. STUART HAYNES

An article that aptly describes the many problems involved in the determination of the mechanism of the photochemical decomposition of acetone has been published by Noyes and Dorfman.[3] Many of their assumptions seem quite valid and well supported but they do not consider this reaction above experimental temperatures of 122°.

In high temperature photolysis of acetone in static systems both Leermakers[4] and Winkler[5] have found that large amounts of methane are formed in the decomposition at 300 to 400°. Allen[6] has made a similar study using a flow system and has also been able to identify methyl ethyl ketone as a product of the reaction using large quantities of acetone. All of these data point to the formation of the acetonyl radical produced in the attack of acetone by methyl radicals. This assumption seems to be generally accepted by these workers but the fate of the acetonyl radical formed has either been assumed to be involved in the formation of methyl ethyl ketone or acetonylacetone or has not been dwelt upon. A consideration of these data causes one to wonder if it would not be possible to obtain reaction conditions in which the fate of the acetonyl radical formed would be its decomposition to form ketene and another methyl radical as in the Rice–Herzfeld mechanism[7] for the pyrolysis of acetone. The work described in this article was undertaken with this question in mind.

As work in static systems necessitates continued exposure of primary products to the ultraviolet radiation and will result in secondary decompositions, a flow system study giving only small percentages of decomposition was chosen. This is of primary importance for Ross and Kistiakowsky[8] have shown that ketene is readily decomposed by ultraviolet radiation, and Williamson[9] has shown ketene to be subject to pyrolytic decomposition at temperatures of 400 to 500°.

Experimental

A diagram of the apparatus used is shown in Fig. 1. The reaction chamber was constructed entirely of fused quartz and had a volume of 200 ml. It was heated and the temperature determined by a temperature controller-recorder manufactured by the Thermal Electric Co. Two traps were placed directly after the reaction chamber to ensure complete condensation or to allow fractional condensation as occasion demanded. Stopcocks on the aniline trap allowed by-passing during evacuation of the system. The last trap in the system was always cooled with a bath of Dry Ice and alcohol to prevent entry of any foreign matter into the pump. The pressure regulator, inserted between the last trap shown and the pump was patterned after a design described by Todd.[10] A Cenco Pressovac pump filled with glycerol to prevent solution of the gases was used to maintain the vacuum and draw the gases into a gas-collecting bottle constructed by connecting the bottom outlets of two 4-l. aspirator bottles. The confining liquid used in these bottles was a solution of 20% sodium sulfate by weight and 5% sulfuric acid by volume in water.

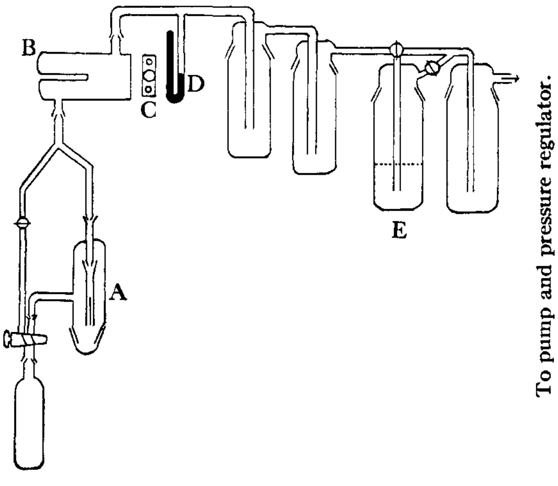

Fig. 1.—Flow system apparatus: A, capillary flow control device; B, quartz reaction chamber with thermocouple well; C, mercury arc lamp; D, manometer; E, aniline trap.

The source of ultraviolet radiation was a General Electric water-cooled mercury arc lamp, type A-H6, with quartz water jacket. This lamp had a power of 1000 watts.

The first two traps in the system were cooled with baths of Dry Ice in alcohol, ice and concd. hydrochloric acid, or iced water, the choice of which is discussed later. Ketene was isolated from the aniline trap in the form of acetanilide. This method of trapping was chosen as it has been shown previously that ketene reacts rapidly and quantitatively with aniline.[11]

The liquids trapped in the various runs were analyzed by means of a Beckman quartz spectrophotometer. Weighed amounts of the liquid were dissolved in 100 ml. of distilled water and the solution diluted volumetrically, if necessary, to give suitable density readings. More detailed discussion of the method of quantitative calculations is discussed in a later section.

Gases were analyzed in a Burrell De Luxe Build-Up Model J gas analysis apparatus. This model was equipped with five absorption pipets, a gas reservoir, copper oxide tube and heater, and catalyst tube and heater. Carbon dioxide was absorbed in a potassium hydroxide solution, ethylene in a solution of bromine water, oxygen in an alkaline solution of pyrogallol, the bulk of carbon monoxide

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[1] From the Ph.D. dissertation of Robert C. Ferris, University of Utah, August, 1949.

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[3] Noyes and Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

[4] Leermakers, THIS JOURNAL, **56**, 1899 (1934).

[5] Winkler, *Trans. Faraday Soc.*, **31**, 761 (1935).

[6] Allen, THIS JOURNAL, **63**, 708 (1941).

[7] Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

[8] Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

[9] Williamson, *ibid.*, **56**, 2216 (1934).

[10] Todd, *Anal. Chem.*, **20**, 1248 (1948).

[11] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 334.

TABLE I

Run	Temp., °C.	Press., mm.	Time of run, min.	Contact time, sec.	Vol. of permanent gases, ml.	Ketene formed, g.	Analyses of gas, %			
							CO	CH_4	C_2H_6	C_2H_4
26	450	100–104	42	7.9	545	0.137	33.2	64.7	0.0	1.8
22	400	96–102	52	10.5	450	.129	43.3	45.6	10.5	0.6
24	350	99–103	60	9.9	330	.145	39.8	37.4	21.7	1.0
28	300	99–103	60	16.6	174	.101	33.0	49.1	17.9	0.0
27	210	99–103	60	13.5	255	.026	40.0	27.6	31.9	0.5

in an acid cuprous chloride solution and the last traces with a Burrell solution known as Cosorbent. Hydrogen was burned in the copper oxide tube and hydrocarbons were analyzed for by catalytic combustion. The confining liquid in this apparatus was mercury.

The acetone in this work was Mallinckrodt analytical reagent grade. The aniline was redistilled under reduced pressure from granulated zinc, b. p. 90° at 30 mm.

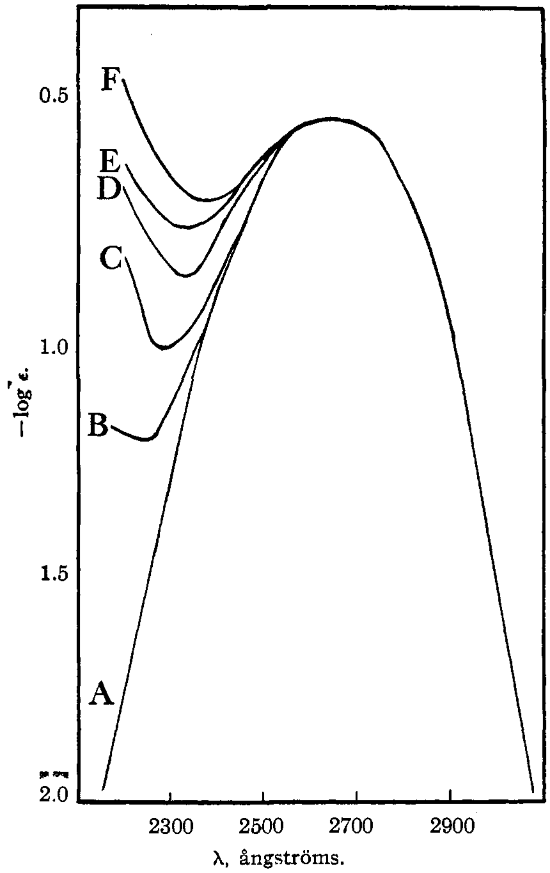

Fig. 2.—Absorption spectra of liquids trapped: ε' = D/cl, where D = optical density, l = cell thickness, c = concn. in g./l. Curve A is for pure acetone. Curve D is for pyrolytically prepared ketene dissolved in acetone.

Curve	Temp. of run, °C.	Baths used: First trap	Baths used: Second trap
B	300	Ice and dil. HCl (about −5°)	Ice and concd. HCl
C	350	Ice and concd. HCl (about −30°)	Ice and concd. HCl
E	400	Ice and concd. HCl	Dry Ice and alcohol
F	350	Ice and concd. HCl	Dry Ice and alcohol

In all cases most of the acetone was condensed in the first trap.

Results

Table I shows experimental conditions and gas analyses for typical runs. All gas analyses were made on an air-free basis. The amount of ketene formed is a combined figure for that found by trapping with aniline and that found by calculations on the ultraviolet absorption spectra of these liquids. Typical spectra are shown in Fig. 2.

Analysis of Liquids by Ultraviolet Absorption Spectra.—It was observed that the extent of the effect of the liquids trapped in raising the absorption curve in the region below 2500 Å. was a function not only of the temperature of the run, because of different rates of ketene formation, but also of the temperature of the cooling bath used to trap out the unreacted material. As shown in Fig. 2, both curves F and C were for runs at 350° in which approximately equal amounts of ketene were formed but which differed by the fact that material for curve F was trapped with a bath of Dry Ice in alcohol whereas material for curve C was trapped with a bath of ice and concentrated hydrochloric acid. That this effect in the spectra was actually due to the presence of dissolved ketene was shown by pyrolyzing acetone at 720°, condensing the substrate and less volatile material in the first trap cooled with Dry Ice in alcohol, isolating the ketene by condensing it in the second trap with liquid air, and dissolving a small amount of it in pure acetone. The spectrum of this solution is shown as curve D.

Also acetanilide was isolated from other photolytic runs by adding an excess of aniline to the liquid trapped and removing the acetone and excess aniline from the mixture by distillation under reduced pressure. In run 26 the condensate was trapped with liquid air and the resulting solution allowed to warm to room temperature before removal from the system. This liquid was added to an excess of aniline and the amount of acetanilide determined quantitatively. Extinction coefficients at various wave lengths were calculated for dissolved ketene from the spectrum of this solution and that of pure acetone. The extinction coefficients thus calculated at 2300 Å. were used to obtain the concentrations of ketene in the other solutions. These calculations were checked by using the calculated concentrations to find values of the optical density at other wave lengths. These values were found to agree with observed values well within experimental error.

TABLE II

Run	Acetone, moles Passed	Acetone, moles Decomposed	Acetone dec., mole %	Moles products per mole acetone dec. CO	CH_4	C_2H_6	C_2H_4	CH_2CO
26	0.146	0.0111	7.6	0.73	1.42	0.00	0.04	0.29
22	.144	.0108	7.2	.85	0.89	.21	.01	.30
24	.189	.0087	4.6	.68	.64	.37	.02	.40
28	.122	.0048	4.0	.53	.79	.29	.00	.50
27	.177	.0055	3.1	.83	.57	.66	.00	.11

Additional data for the runs reported are shown in Table II. The number of moles of acetone decomposed was calculated from the sum of the weights of products found as this was believed to be the most accurate method of measuring this quantity. This necessarily assumes that all of the products have been caught and identified separately from the condensed acetone. The sums of the moles of oxygen-containing products per mole of acetone decomposed are 1.02, 1.15, 1.08, 1.03 and 0.94, respectively. It is felt that the maximum error is not unreasonable in view of the difficulty of accurate gas analyses and the magnification of error caused by converting the experimentally determined values to a mole per mole basis. Run 22 is the only one of these runs that seems to give an error of undesirable magnitude. Carbon balances based on data in Table II together with a consideration of reactions proposed in the Discussion section (*vide infra*) give even better agreements than those above. This table also shows that the mole per mole amount of ketene formed increases with decrease in temperature down to 300°, with a rapid falling-off below this value. The temperature of 210° was the lowest which could be maintained constant in the apparatus used.

Discussion

The effect of temperature on the photolysis of acetone has been found in this work to be essentially the same as in previous studies. Large amounts of methane are present in the gaseous products at the higher temperatures and this component decreases with decreasing temperature. The amount of ethane found does not follow such a smooth relationship, however. As ethane formation is probably a heterogeneous reaction, other factors than the temperature come into play in its production. It has been found in this work generally that the relative amount of ethane formed can be kept to quite a small value by taking extra precautions in cleaning the reaction vessel before making a run. A carbonaceous deposit appears in the reaction vessel during a given run and its effect on the following run appears to be an increase in ethane formation. This observation fits well with the over-all mechanism proposed for this reaction below.

Possible Mechanisms.—The authors of this paper felt that there should be some connection between the photolysis of acetone and its pyrolysis, in spite of the fact that ketene is a well-known product of the pyrolytic decomposition but had not been found as the result of photolysis investigations. When absorption of a quantum causes rupture of an acetone molecule the resulting fragments should exhibit a variety of behavior patterns that depend upon several factors, including concentration, contact time and temperature. If conditions are right it is reasonable to expect some of these fragments to attack the substrate molecules, removing a hydrogen atom from one of them and forming an acetonyl radical. Again under proper conditions, this radical should then be able to decompose to give rise to ketene and initiate a chain reaction typical of the Rice–Herzfeld mechanisms[7] for pyrolyses. Possible alternative steps include

$$CH_3COCH_3 = CH_3CO + CH_3 \qquad (1)$$
$$CH_3CO = CH_3 + CO \qquad (2)$$
$$CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2 \qquad (3)$$
$$CH_3COCH_2 = CH_3 + CH_2{=\!=}C{=\!=}O \qquad (4)$$
$$CH_3 + CH_3 = C_2H_6 \qquad (5)$$
$$CH_3 + CH_3COCH_2 = CH_3COC_2H_5 \qquad (6)$$
$$CH_3COCH_2 + CH_3COCH_2 = CH_3COCH_2CH_2COCH_3 \qquad (7)$$
$$CH_3CO + CH_3CO = CH_3COCOCH_3 \qquad (8)$$
$$CH_3CO + CH_3COCH_2 = CH_3COCH_2COCH_3 \qquad (9)$$
$$CH_3CO + CH_3COCH_3 = CH_3CHO + CH_3COCH_2 \qquad (10)$$

Of these, the first five or six reactions constitute a Rice–Herzfeld mechanism with steps 3 and 4 making up the chain. Reactions 8, 9 and 10 can occur only if the conditions permit some degree of stability to the acetyl radical. In their photolyses of acetone in a static system at room temperature Spence and Wild[12] obtained biacetyl but reported that at 60° it was not formed. Certainly at the temperatures of the present work the acetyl radical would be quite unstable and the products formed by the last three reactions would not be expected nor was there any indication of their formation.

Reaction 3 may have a sufficiently high activation energy so that it does not occur at room temperature, in which case the methyl radicals would unite in pairs and the only hydrocarbon obtained would be ethane. According to the work of Spence and Wild[12] and Herr and Noyes[13] this appears to be the situation at room temperature. However, in their runs at 60° the first of these authors found appreciable amounts of methane appearing in the gaseous products. With conditions permitting reaction 3 the question arises as to the fate of the acetonyl radical thus formed. Allen[6] showed that only about 0.3 ml. of methyl ethyl ketone is formed at 380° by passing 187.5 ml. of acetone through a flow system in fifty-seven hours, this presumably by reaction 6. Two other alternatives for the disposition of the acetonyl radical are indicated by reactions 4 and 7. There is nothing in this work to support the formation of acetonylacetone in any appreciable amounts.

The products obtained here indicate that the chain reaction giving ketene occurs to a considerable extent from temperatures ranging from 450

(12) Spence and Wild, *J. Chem. Soc.*, 352 (1937).

(13) Herr and Noyes, THIS JOURNAL, 62, 2052 (1940).

down to 200°. Winkler[5] stated that ketene may have been formed in his photolysis of acetone at 300 to 400° because of the formation of a film of brown condensate on the inner surface of his reaction chamber and the presence of unsaturated compounds in his gaseous products, but he made no tests to prove that ketene had been formed. Our results show that the production of ketene in relatively large amounts should be taken into account under the conditions of our photolyses.

Competing Over-all Reactions That Satisfy the Relative Amounts of Each Product Obtained.—Some difficulty was encountered in attempting to explain the formation of more than one mole of methane per mole of acetone decomposed found in run 26 (see Table II). A similarly large ratio had been obtained in two previous runs carried out at the higher temperatures so that this result was corroborated. The two obvious competing reactions for the photolysis are

$$CH_3COCH_3 = CH_4 + CH_2{=}C{=}O \qquad (11)$$

$$CH_3COCH_3 = C_2H_6 + CO \qquad (12)$$

If these were the only two involved the moles of methane per mole of acetone decomposed could never be greater than one and the yield of methane and of ethane should be the same, respectively, as those of ketene and of carbon monoxide within experimental error. Reference to Table II shows that the latter relationships do not hold for our results.

An equation for the pyrolytic decomposition of ketene has been proposed by Williamson[9] and also by Hurd and Williams.[14] This is

$$2CH_2{=}C{=}O = CH_4 + C + 2CO \qquad (13)$$

By assuming that some of the ketene produced in our experiments was decomposed by such an overall reaction, equations 11 and 13 may be combined to get a third over-all reaction for the decomposition of acetone, *viz.*

$$2CH_3COCH_3 = 3CH_4 + C + 2CO \qquad (14)$$

Use of equation 14 could explain the relatively large quantities of methane obtained in runs at 450°. The combined use of equations 11, 12 and 14 gives surprisingly satisfactory agreement with our experimental mole per mole ratios obtained at *all* temperatures used.

TABLE III

Run	CH_4/ CH_2CO	C_2H_6/ CH_2CO	CH_4/Acetone		CO/Acetone		C_2H_6/ Acetone	
			Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.
26	4.84	0.00	1.36	1.42	0.72	0.73	0.00	0.00
22	2.98	.69	0.99	0.89	.67	.85	.23	.21
24	1.60	.93	.69	.64	.57	.68	.40	.37
28	1.59	.59	.80	.79	.50	.53	.30	.29
27	5.17	6.00	.53	.57	.90	.83	.62	.66

Table III shows how this was done and compares the results obtained by calculation from these three equations with those found experimentally. To illustrate, in the case of run 24 there were 1.60 moles of methane obtained experimentally for each mole of ketene. Equation 11 gives one mole of methane for each of ketene so that equation 14 is given a weight of 0.60/3 = 0.20 compared to a weight of 1.00 for equation 11. As there was 0.93 mole of ethane formed in this run for each mole of ketene, equation 12 is given a weight of 0.93. Addition of these three equations, weighted in this manner, gives

$$2.33CH_3COCH_3 = 1.60CH_4 + CH_2{=}C{=}O + 0.93C_2H_6 + 1.33CO + 0.2C$$

The calculated values given for run 24 in Table III are obtained directly from this summation of the weighted equations. Similarly, the other calculated values of this table were found for the other runs. The coincidence of agreement shown in Table III speaks for itself.

In addition to the comparison of observed and calculated values for the ratios in Table III, carbon balances have been calculated. Three gram atoms of carbon must be present in the products for each mole of acetone decomposed. From one mole of acetone decomposed it is found that the gram atoms of carbon total 3.17, 3.00, 2.99, 3.00, 3.08, in the same order of presentation as in Tables II and III. The maximum error involved here is certainly not unreasonable. To illustrate this calculation, also in the case of run 24 and using the data of Table II, the gram atoms of carbon present altogether in the products are 0.68 for carbon monoxide, 0.64 for methane, 2 × 0.37 (= 0.74) for ethane, 2 × 0.02 (= 0.04) for ethylene, 2 × 0.40 (= 0.80) for ketene; for elementary carbon, due to the lack of experimental values, one must use the value of 0.2/2.33 (= 0.09) obtained from the equation derived in the paragraph above. The addition of these figures gives 2.99.

It is not our intention to claim that equations 11, 12 and 14 are the only competing equations that could be made to fit our data reasonably well, but in view of the fact that 11 and 12 are generally acceptable, the coincidence obtained by using 14 with them is startling. As would be expected, the weight given equation 14 diminishes from 1.3 for run 26 at 450° to 0.20 for run 28 at 300°. The high weight of 1.39 for equation 14 in run 27 at 210° is explainable. At this low a temperature, reaction 4 has slowed up appreciably so that relatively little ketene is produced. Thus a relatively large amount of the ketene formed may be further decomposed to give the products of equation 14 and in so doing increase the yield of methane. It would then become necessary to explain the fate of the acetonyl radicals that are formed by reaction 3 but do not undergo the decomposition to give ketene. It is logical to assume that these radicals may combine with some of the methyl radicals to give methyl ethyl ketone. The presence of this product in the relatively large quantities of condensed substrate would be difficult to show by use of the ultraviolet spectrophotometer because

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[14] Hurd and Williams, THIS JOURNAL, 58, 962 (1936).

of the similarity in the spectra of the two substances. In this connection it is interesting that the sum of the moles of carbon monoxide and of ketene is less than one only in the case of run 27. The values given in Table III for this run give good agreement, however, which may be taken as an indication that the amount of methyl ethyl ketone formed in this run is small.

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Summary

The present investigation points out a number of facts that should prove of importance in the study of this and other photochemical reactions.

1. Ketene is formed in the photolysis of acetone in a flow system under the proper conditions and at temperatures much lower than those required for its preparation by pyrolysis. This is of importance in view of the assumption at the time of the publication of Noyes and Dorfman[3] that all of the products were known.
2. Ultraviolet spectra have been found useful in identifying and measuring ketene trapped with unreacted acetone.
3. Competing over-all reactions are proposed to fit the relative quantities of products obtained in the high temperature photolysis of acetone.
4. A flow system for photochemical studies has the same relative advantages as for pyrolytic work, enabling the detection of primary products.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Kinetics of the Iodine–Iodate Isotopic Exchange Reaction

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The exchange of iodine atoms between aqueous iodine and iodate ion has been reported as being a slow reaction.[2] Radioactive I^{131} has been used in the present investigation in order to obtain the quantitative dependence of the exchange rate on concentrations of both exchange reactants and hydrogen ion and on the temperature. It is assumed that I^{131} behaves chemically[3] as does I^{127}.

The iodine–iodate exchange, with the exchange rate R, may be studied by the use of the radioactive I^{131} tracer

$$II^{131} + IO_3^- = II + I^{131}O_3^-$$

The exchange rate, a function of the total concentrations and temperature, follows the general law for a first order reversible reaction, given by[4]

$$R = \frac{2\{I_2\}\{IO_3^-\}}{2\{I_2\} + \{IO_3^-\}}\,\frac{\ln 2}{T_{1/2}}$$

The braces are used to denote formal concentrations expressed in gram-formula weights of the enclosed species per liter of solution, and $T_{1/2}$ represents the time required for the exchange to proceed half of the way to equilibrium. At complete exchange the specific activities of both reactants will be identical. A graph of log (1 − fraction exchange) against time will give a straight line from which the value of the "half-time" may be obtained.

If a single exchange path is operative, then by varying the concentrations of the reactants in separate experiments one can evaluate the order of the mechanism. At a given temperature R will be given by

$$R = k_T\,(I_2)^m(IO_3^-)^n(H^+)^p\Gamma$$

where parentheses are used to indicate actual concentrations of a particular species in moles or gram-ions per liter, and Γ includes the activity coefficients of the reactants and the transition state raised to the appropriate powers. We shall distinguish between actual concentrations of a species and formal concentrations expressed in gram-formula weights per liter of solution.

The activity of iodic acid can be held at a constant value for a series of experiments at constant temperature. Then from a determination of the exchange rate at various iodine concentrations a plot of log R *vs.* log (I_2) will yield a straight line with a slope equal to the iodine dependence m. The use of iodine concentrations is permissible because the activity coefficient for this neutral species is approximately constant over the range of concentrations used. If there is in this concentration range an alternate path involving a different value of m the slope of log R *vs.* log (I_2) will not be constant. We have attempted to evaluate m, n and p, the orders of the exchange reaction with respect to iodine, iodate ion and hydrogen ion.

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[1] The material herein presented constitutes a part of the Ph.D. thesis of O. E. Myers, Monsanto Fellow, Washington University, June, 1949. Present address of Mr. Myers is Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[2] Hull, Shiflett and Lind, THIS JOURNAL, **58**, 535 (1936); Polessitsky, *Compt. rend. acad. sci., U. R. S. S.*, **24**, 540 (1939); Cottin and Haïssinsky, *Compt. rend.*, **224**, 1536 (1947).

[3] According to partition function calculations by Urey, *J. Chem. Soc.*, 562 (1947), we may expect equilibrium constants differing by only about 0.5% for these two isotopes in the iodine–iodate equilibrium.

[4] McKay, *Nature*, **142**, 997 (1938); Duffield and Calvin, THIS JOURNAL, **68**, 557 (1946); Friedlander and Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, New York, N. Y., 1949.