

Another expansion for ϕ is demanded at low pressures, and the leading term of this contains the light intensity to the minus one-half power as required by the data at low pressures.

The slight effect of added nitrogen may be explained by reaction (8) leading to a decreased concentration of the primary free radicals. It is not surprising that oxygen is used up in the reaction since such a reaction as $H + O_2 = HO_2$ and others can set up chains.

Although the splitting off of a methyl group and a hydrogen to form methylacetylene has been shown not to take place, the formation of allene by removal of a hydrogen from R_3 simultaneously with or following (4) is not excluded by the data. Removal of a methyl group from R_4 likewise can produce allene.

Summary

1. The effect of approximately monochromatic radiation from the aluminum spark, about 1900 Å., on isobutene has been investigated. Both decomposition and polymerization occur, and in re-

gion of maximum rate the data are summarized by the following quantum yields: hydrogen, 0.03; methane, 0.10; hydrocarbon with 2.25 carbon atoms per molecule, 0.16; polymer with 9.05 carbon atoms per molecule, 0.45.

2. A free radical mechanism is required for some of the processes and, moreover, is capable of accounting for all the observed processes. The essential features are: at low pressures, the most important reactions are splitting of the excited isobutene molecule into primary free radicals which recombine in the gas phase and on the wall, some of them reacting with isobutene molecules. At higher pressures, the excited molecules are quenched to a large extent, the radicals which are formed reacting chiefly with isobutene to form other radicals which eventually combine.

3. The nature of the wall is shown to influence the reaction.

4. No methylacetylene could be found so that little analogy with the effect of light on ethylene exists.

PROVIDENCE, R. I.

RECEIVED SEPTEMBER 26, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Conductance of Potassium Iodate at 25° and the Mobility of the Iodate Ion

BY K. A. KRIEGER AND MARTIN KILPATRICK

The conductance of potassium iodate at 25° has been measured by Walden, by Harkin and Pearce, and by Kraus and Parker.¹ The measurements of Harkins and Pearce, and Kraus and Parker are unfortunately rather incomplete, only four concentrations having been studied. Walden's work, while much more extensive, is probably not highly accurate.

As will be shown later all previous values of the mobility of the iodate ion at 25° depend ultimately upon Kraus and Parker's¹ measurement of the conductance of iodic acid. Unfortunately any attempt to calculate iodate ion mobility from these data is handicapped by the fact that the mobility of the iodate ion appears as the small difference between the large conductances of iodic acid and hydrogen ion.

For these reasons it has seemed of interest to

repeat and extend the earlier measurements of the conductance of potassium iodate.

Experimental

Potassium iodate (Baker special reagent) was twice recrystallized from conductivity water, and two successive crops of crystals were collected. Spectroscopic examination of both crops showed the absence of foreign metals except traces of sodium, and the usual test for iodides² indicated the presence of less than 0.01% iodide, calculated as potassium iodide. Samples of the purified salt were heated to constant weight in a vacuum at 110–115°.

The apparatus and technique employed have been described in an earlier paper.³

The Density of Potassium Iodate Solutions.—The densities of two solutions of potassium iodate

(1) Walden, *Z. physik. Chem.*, **2**, 49 (1888); Harkins and Pearce, *THIS JOURNAL*, **38**, 2679 (1916); Kraus and Parker, *ibid.*, **44**, 2429 (1922).

(2) Rosin, "Reagent Chemicals and Standards," D. Van Nostrand Co., New York, N. Y., 1937, pp. 332–333.

(3) Krieger and Kilpatrick, *THIS JOURNAL*, **59**, 1878 (1937).

were measured and found to agree within the experimental error with those reported in the literature.⁴ The equation

$$d = 0.99707 + 0.00847 C$$

where d is the density of C per cent. potassium iodate solution, is correct to 0.01% up to about 0.1 molar.

The Conductance of Potassium Iodate.—Table I records the conductance of the potassium iodate solutions. In this table, c is the concentration in gram equivalents per liter, corrected for the conductance of the solvent, Λ_x is the observed equivalent conductance, and Λ_1 , Λ_2 , Λ_3 are equivalent conductances as calculated by the equations discussed below.

TABLE I

c	Λ_x	Λ_1	Λ_2	Λ_3
0.0		113.96	113.95	114.00
b .00010301	113.56 ⁵	113.08		
a .00013079	113.03	112.98	112.98	113.02
c_1 .00044864	112.31	112.16	112.17	112.20
c_2 .0010303	111.44	111.25	111.27	111.28
d_1 .0015476	110.73	110.65	110.68	110.68
c_3 .0028690	109.52	109.49	109.54	109.53
d_2 .0035645	109.01	109.00	109.06	109.04
d_3 .0049183	108.17	108.16	108.23	108.20
d_4 .0061882	107.49	107.51	107.57	107.54
c_4 .0063964	107.38	107.41	107.47	107.41
d_5 .0070663	107.06	107.10	107.14	107.11
e_1 .010067	105.76	105.88	105.90	105.87
d_6 .022640	102.18	102.26	102.19	102.24
e_2 .031087	100.42	100.52	100.39	100.48
e_3 .058800	96.35	96.35	96.12	96.28
e_4 .10126	92.24	92.12	92.33	92.07

Specific conductance of water, $\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-7}$

Run	a	b	c	d	e
	4.13	5.37	1.65	10.53	2.27

Discussion

The choice of a suitable value for Λ_0 is a matter of some difficulty and several methods of plotting the data have been tried.

(1) The seven values of Λ corresponding to concentrations less than 0.005 g. equivalent per liter (point b omitted) were plotted against the square root of the concentration. This procedure yields a very good straight line, and the application of least squares gives an intercept of 114.05 and a slope of -83.88 . According to Onsager's equation⁶ the slope should be -86.42 , but this deviation is not large enough to be significant.

(4) "International Critical Tables," Vol. III, p. 87.

(5) Run b was spoiled by an accident and the value given above has been omitted from all subsequent calculations.

(6) Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

(2) The constants Λ_0 and B of Shedlovsky's⁷ equation

$$\Lambda_0' = \Lambda_0 + Bc \quad (\text{A})$$

were determined by extrapolation. A plot of

$$\Lambda_0' = \frac{\Lambda + 60.27 \sqrt{c}}{1 - 0.2294 \sqrt{c}} \text{ vs. } c$$

is convex to the c axis, and shows very clearly that the value of Λ_0 so obtained is too low, and that B varies with the concentration range selected. If we assume $\Lambda_0 = 113.96$, $B = 60.3$ then the values given under Λ_1 in Table I are obtained. The fit is not as good as might be expected and the deviations are systematic.

(3) Since it has been pointed out⁸ that terms of the form $c \log c$ and c^2 (as well as c) were omitted in Onsager's original equation, we have applied the method of least squares to the data of Table I, calculating the constants Λ_0 , B , D and E in the equation

$$\Lambda_0' = \Lambda_0 + Bc + Dc \log c + Ec^2$$

with the result

$$\Lambda_0' = 113.95 + 2.38c - 29.0c \log c + 309.6c^2$$

Values of Λ obtained from this equation are given under the heading Λ_2 . The agreement obtained with this equation over the whole range is not quite as good as with Shedlovsky's equation (A), although the fit is better for the higher concentrations.

(4) If $\Lambda_0 = 114.00$ and $B = 60.6$ are chosen arbitrarily we may write

$$N = 114.00 + 60.6c$$

and

$$X = \Lambda_0' - N$$

We have calculated the values of X corresponding to each value of c and applied the method of least squares to the equation

$$X = Dc \log c + Ec^2$$

obtaining

$$D = 2.44 \text{ and } E = 21.5 \text{ or}$$

$$\Lambda_0' = 114.00 + 60.6c + 2.44c \log c + 21.5c^2$$

and the values so calculated are given under the heading Λ_3 . The agreement over the whole range is approximately the same as that given by Shedlovsky's equation.

On the basis of these calculations, we have chosen $\Lambda_0 = 114.00 \pm 0.05$.

(7) Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1932). The numerical quantities in this equation have been recalculated to conform with the following constants: $e = 4.805 \times 10^{-10}$ e. s. u., $0^\circ\text{C.} = 273.18^\circ\text{K.}$, $N = 6.025 \times 10^{23}$, $K = 1.380 \times 10^{-16}$, D (water at 25°C.) = 78.54.

(8) Onsager, ref. 6; Fuoss, *Physik. Z.*, **35**, 59 (1934).

The Conductance of the Iodate Ion.—McDougall and Davies⁹ using the data of Kraus and Parker, gave 40.93 as the conductance of the iodate ion on the Kohlrausch and Maltby standard, or about 40.89 on the Jones and Bradshaw standard.¹⁰ More recently, however, Davies¹¹ has pointed out that from the data of Kraus and Parker on the conductance of iodic acid, and of Longworth¹² on the mobility of the hydrogen ion, the figure 41.00 is obtained for the iodate ion. On the other hand, Kraus and Parker themselves reported 39.59 (Jones and Bradshaw standard) on the basis of their own measurements of iodic acid

(9) McDougall and Davies, *J. Chem. Soc.*, 1417 (1935).

(10) Jones and Bradshaw, *THIS JOURNAL*, **55**, 1780 (1933); Davies, *J. Chem. Soc.*, 1326 (1937).

(11) Davies, private communication.

(12) Longworth, *THIS JOURNAL*, **54**, 2741 (1932).

and some rather incomplete measurements of potassium iodate.

If we accept the value $\Lambda_{0KIO_3} = 114.00 \pm 0.05$ and make use of the data of Shedlovsky¹³ for $\Lambda_{0KCl} = 149.86$ and $\lambda_{0Cl^-} = 76.34$ (all on Jones and Bradshaw standard) then $\lambda_{0IO_3^-} = 40.48 \pm 0.05$.

Summary

1. The conductance of potassium iodate has been measured over the range 0.0001 to 0.1 molar in water at 25°.

2. The mobility of the iodate ion at infinite dilution has been calculated from the conductance of potassium iodate and potassium chloride and the mobility of the chloride ion.

(13) Shedlovsky, *ibid.*, **54**, 1405 (1932).

PHILADELPHIA, PA.

RECEIVED OCTOBER 20, 1941

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 253]

New Methods for Investigating the Distribution of Ethoxyl Groups in a Technical Ethylcellulose¹

BY JOHN F. MAHONEY² AND C. B. PURVES

Although the average degree of substitution and the average molecular weight of partly alkylated cellulose chains can be determined with considerable certainty, the exact mode of distribution of the substituent within the cellulose molecule remains largely unknown. The means of separating and analyzing the mixtures of partly alkylated glucoses obtained by degradation are not yet accurate enough to determine the average distribution within the glucose residues and are only of very slight value in estimating distribution along the chain. Much valuable and semi-quantitative work, however, has been done on this subject and a few of the literature references are appended.^{3-7a} The fractionation of partly alkylated celluloses has provided little information beyond the fact that the more soluble, shorter

chain length fractions tend to be rather more highly substituted than the original material.^{5,8-14} Studies on the course of alkylation,^{4,15} on the mathematical analysis of the kinetics of the reaction¹⁶ and on correlations between physical properties and the extent and mode of distribution^{17,18} have accordingly been hampered by a lack of quantitative data. The present article and the succeeding one attempt to mitigate this deficiency.

In the case of simple glycosides, heating the *p*-toluenesulfonyl (tosyl) esters of primary alcohol groups with sodium iodide in acetone gives a quantitative yield of the corresponding iodoglycoside whereas esters of secondary alcohol groups are unaffected.^{19,7b} This method of estimating primary in the presence of secondary hydroxyl groups was successfully used to differen-

(1) Presented before the Division of Cellulose Chemistry at the Atlantic City meeting of the American Chemical Society, September, 1941.

(2) Abstracted from a thesis submitted by J. F. Mahoney to the Faculty of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941. Present address: Merck and Company, Rahway, New Jersey.

(3) Denham and Woodhouse, *J. Chem. Soc.*, **111**, 244 (1917).

(4) Hess, Trogus, Eveking and Garthe, *Ann.*, **506**, 260 (1933).

(5) Hess, *ibid.*, **506**, 295 (1933).

(6) Heddle and Percival, *J. Chem. Soc.*, 249 (1939). This article gives other references.

(7) Compton, *THIS JOURNAL*, (a) **60**, 2823, (b) 1203 (1938).

(8) Denham, *J. Chem. Soc.*, **119**, 77 (1921).

(9) Heuser and Heimer, *Z. Elektrochem.*, **32**, 47 (1926).

(10) Okamura, *Cellulosechem.*, **14**, 135 (1933).

(11) Ubbelohde, *ibid.*, **14**, 169 (1934).

(12) Lee and Sakurada, *J. Soc. Chem. Ind. Japan*, **38**, Supp. Binding, 436 (1935); *C. A.*, **29**, 8323 (1935).

(13) Signer and Liechti, *Helv. Chim. Acta*, **21**, 530 (1938).

(14) Staudinger and Reinecke, *Ann.*, **535**, 47 (1938).

(15) Lorand and Georgi, *THIS JOURNAL*, **59**, 1166 (1937).

(16) Spurlin, *ibid.*, **61**, 2222 (1939).

(17) Lorand, *Ind. Eng. Chem.*, **30**, 527 (1938).

(18) Ott, *ibid.*, **32**, 1641 (1940).

(19) Oldham and Rutherford, *THIS JOURNAL*, **54**, 366 (1932).