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The Photochemistry of Isobutene. I¹

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Introduction

Isobutene in common with many other unsaturated compounds has been observed to polymerize under a variety of conditions.³ In a condensed phase, most of the polymerization reactions proceed in such a way as to make attractive a mechanism involving activated molecules which add to normal molecules. Likewise, in the vapor phase, the photochemical reactions of the acrylates⁴ and the mercury sensitized polymerization of butadiene⁵ have been regarded as also proceeding by way of an activated molecule mechanism.

On the other hand, the photochemical and sensitized reactions of the simpler unsaturated hydrocarbons such as ethylene, acetylene, and others⁶ appear to be capable of no straightforward explanation. The actual presence of free radicals

and atoms is quite clearly indicated, however, and a large variety of intermediate atoms, molecules, and radicals must exist.

This investigation was undertaken to observe the direct action of light on the isobutene molecule and in particular to attempt to determine the mechanism of its gas phase photochemical polymerization.

The ultraviolet absorption spectrum of isobutene has been investigated by Carr and Stucklen.⁷ Absorption begins in the neighborhood of λ 2000 Å. and extends into the ultraviolet, maxima of absorption appearing at $\lambda\lambda$ 2018, 1935, 1887 and 1840 Å. These authors agree with Mulliken that in the notation of the latter the transition involved is of the type $[X + X] \rightarrow [X - X]$. This means the transfer of an electron associated with the carbon-carbon double bond from a bonding orbital to an antibonding orbital. It might possibly be expected that such an excited molecule could add to an unsaturated molecule, thereby setting up an activated molecule mechanism similar to that postulated in the case of butadiene⁵ or the acrylates.⁴ The results of this investigation tend to make this appear unlikely, however. In fact, a primary process involving dissociation into free radicals seems more probable.

Experimental

The apparatus was of a sort commonly used in photochemical work. A light source was focused by quartz lenses through a quartz reaction cell connected to a vacuum

(1) This article is based on a thesis submitted by William F. Kieffer in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

(2) Jesse Metcalf Fellow in Chemistry at Brown University, 1939-1940: Present address, The College of Wooster, Wooster, Ohio.

(3) (a) Lebedev and Koblyanskii, *Ber.*, **63B**, 1432 (1930); (b) Steacie and Shane, *Can. J. Research*, **16B**, 210 (1938); (c) Roper, *THIS JOURNAL*, **60**, 2699 (1938); no attempt to cover all of the work on polymerization of isobutene is made here.

(4) Melville, *Proc. Roy. Soc. (London)*, **A163**, 511 (1937); Melville, *ibid.*, **A167**, 99 (1938).

(5) Gee, *Trans. Faraday Soc.*, **34**, 712 (1938).

(6) (a) Mooney and Ludlam, *Trans. Faraday Soc.*, **25**, 442 (1929); (b) McDonald and Norrish, *Proc. Roy. Soc. (London)*, **A157**, 480 (1936); (c) Rice and Sickman, *THIS JOURNAL*, **57**, 1384 (1935); *J. Chem. Phys.*, **4**, 608 (1936); (d) Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937); (e) Joris and Jungers, *Bull. Soc. Chim. Belg.*, **47**, 135 (1938); (f) Olson and Meyers, *THIS JOURNAL*, **48**, 389 (1926); (g) Bates and Taylor, *ibid.*, **49**, 2438 (1927); (h) Lind and Livingston, *ibid.*, **54**, 94 (1932); *ibid.*, **55**, 1036 (1933); (i) Taylor and Jungers, *J. Chem. Phys.*, **4**, 94 (1936); (j) Steacie and others, see paper given before New York Academy of Sciences Conference on Photochemistry, May 3 and 4, 1940.

(7) Carr and Stucklen, *J. Chem. Phys.*, **4**, 760 (1936).

system in which the material could be purified and analyses made.

Light Source.—Since isobutene absorbs strongly in the region $\lambda\lambda 2000-1800$, a convenient source of radiation was the aluminum spark. Power was supplied by two 25,000 volt, 1 kilovolt-ampere Thordarson transformers connected in parallel to two aluminum disks (five inches in diameter) which were rotated slowly at right angles to one another by two synchronous clock motors. One of the electrodes and its motor was mounted so that the spark gap could be regulated to constant width. A glass plate condenser of approximately 0.015 mfd. capacity was connected across the spark. The whole electrode assembly was housed in a transit box lined with celotex and connected to a ventilating system. A group of lines consisting of the following: $\lambda\lambda 1854.67, 1858.15, 1862.48, 1862.9, 1930.3, 1935.2, 1989.8 \text{ \AA.}$, was isolated by the method of focal isolation. This light source proved to be reasonably constant. Its intensity was varied when desired by placing blackened wire screens in the path, or by changing the voltage impressed on the spark.

Measurements of relative light intensity were made with a photoelectric cell in a quartz envelope. For the determination of quantum yields, the photocell was calibrated by means of a Moll multiple junction surface thermopile which in turn was standardized against a Bureau of Standards lamp. Partly because of the fact that the relative intensities of the lines from the aluminum spark were only approximately known, an uncertainty remained in the determination of the number of quanta. It was estimated that the error of a calibration was not more than 4%.

The fraction of the radiation absorbed by the isobutene was measured directly with the photoelectric cell.

Materials.—Isobutene was prepared from isobutyl alcohol by a method similar to that of Komarewsky.⁸ It was fractionated in a small column of the Podbielniak type and a fraction boiling at $-6.6 \pm 0.1^\circ$ collected and stored. Samples were admitted to the system from the storage bulb cooled to dry-ice temperatures. A tube packed with activated alumina served to dry the gas further. Distillations from dry-ice to liquid air temperatures were repeated in the vacuum system to ensure the removal of any polymer which might have formed on standing.¹⁰

For particular experiments, nitrogen and oxygen were admitted to the system from a tank through a trap containing calcium chloride at dry-ice temperatures to remove water vapor.

Measurement of Pressure Changes.—A fairly sensitive pressure gage was constructed from a Hydron brass bellows of the extra flexible type. The balancing pressure was read from a manometer containing Apiezon oil by means of a cathetometer. Pressure changes could be read reproducibly to 1.5×10^{-3} mm. of mercury directly from the gage.

Analyses.—After irradiation a rough fractionation process was carried out as follows. A copper block containing two wells, one for a trap on the reaction system, and the other for a pentane thermometer, was placed over a condensation trap. The block was completely immersed in liquid air and a first fraction (I) of gas removed from that part of the system with a Toepler pump. By lowering the

Dewar flask containing liquid air, the temperature of the block was raised to -145° , whereupon a second fraction (II) was removed with the Toepler pump. This temperature was chosen as the maximum which would just prevent removal of isobutene. These two fractions taken together were termed the non-condensable gas. The isobutene was removed by pumping with the trap at a temperature of -110° . When the pressure had been reduced to approximately 10^{-4} mm. of mercury, the polymeric residue, fraction III, was volatilized, and its pressure measured with the bellows gage.

The fractions were analyzed successively in the following manner: hydrogen, by oxidation over copper oxide; unsaturated hydrocarbons, by catalytic hydrogenation over copper made by freshly reducing the oxide; hydrocarbons, by combustion with oxygen. It was not considered worthwhile to analyze the isobutene fraction. The method of Mooney and Ludlam^{8a} was used to detect acetylenic compounds if present. The isobutene flowed through a small quartz cell into ammoniacal cuprous chloride solution. Methylacetylene, if present, should form an insoluble greenish-yellow copper salt.⁹ No precipitate was observed after irradiating the cell for fifty minutes. Under the same condition, ethylene produced a precipitate of copper acetylide in less than one minute.

The analytical procedure leaves much to be desired as far as accuracy is concerned, but it proved to be well suited to the introductory work on the problem.

Effect of Walls.—The nature of the walls was changed for a series of reactions by evaporating a film of lead on the interior of the reaction cell. Care was taken to leave the front window completely clear.

Fluorescence.—Attempts were made to observe possible fluorescence by placing a photographic plate so as to intercept radiation scattered at right angles to the beam of exciting light. No difference in scattered light could be observed with the cell empty or filled with isobutene to pressures in the neighborhood of 0.2 mm.

Results

The fraction of the radiation absorbed by isobutene at different pressures is shown in Table I. Due to the nature of the radiation, it consisting of bands in addition to the strong aluminum lines, and the nature of the absorption, it is not possible

TABLE I

Pressure, mm.	I/I_0	Pressure, mm.	I/I_0
0.022	0.94	0.221	0.58
.035	.92	.289	.48
.049	.87	.381	.39
.077	.84	.477	.36
.110	.79	.525	.27
.114	.77	.677	.26
.115	.77	1.22	.17
.125	.76	1.37	.15
.143	.70	2.19	.14
.210	.60	4.36	.13
.213	.61	4.70	.11

(9) Beilstein, "Handbuch der organischen Chemie," III Auf. Bd. I, p. 129.

(8) Komarewsky, THIS JOURNAL, 56, 2705 (1934).

to represent these data with any simple expression of the usual type.

Figure 1 shows microphotometer tracings of the aluminum spark spectrum and the absorption spectrum of isobutene superposed. The spectrograms were photographed with a one meter vacuum grating.

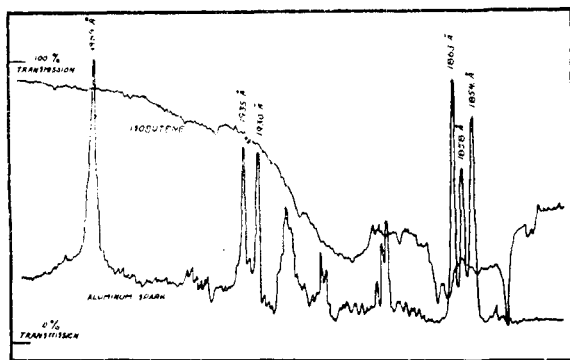


Fig. 1.

Rate Measurements.—Figure 2 shows the pressure decrease as measured with the bellows gage plotted as a function of time at a constant light intensity of approximately 11×10^{15} quanta per minute. Even though the cell was swung out of the beam at ten, twenty, thirty and forty minutes, no discontinuities appear in the curves except with added oxygen. Thus there is no dark reaction except in the latter case. Moreover, no induction period is present. Only a portion of the total number of rate curves taken is shown in Fig. 2. For initial pressures between 16 and 30 mm. the rate changed very little. As the pressure was increased beyond this range, the rate decreased gradually. From the initial slope of these curves a quantum yield for pressure decrease could be calculated. Figure 3 shows these results.

Although it might be preferable to give quantum yields for the formation of various products as a function of the pressure, the analyses are not accurate enough to show any pressure dependence. Average values are probably reliable, however, and these are applicable over the pressure range in which the quantum yields are essentially constant. The quantum yield for non-condensable gas formation

could be measured directly, and is shown in Fig. 3. The amount of polymer could be measured with considerably less accuracy since several partial evaporations and final measurements of pressure with the bellows gage were necessary, whereas the non-condensable gas was measured with the McLeod gage. However, since the number of molecules of polymer could be determined more or less directly, the quantum yield for its formation is shown over a limited pressure range in Fig. 3. The ratio of the pressure of polymer formed to net pressure decrease averaged 0.90.

In Fig. 4 are plotted the ratios of non-condensable gas formed to actual pressure decrease for a clear cell, and for one in which a film of lead covered all walls except the front window.

The results of analyses showed no regular variation with pressure over a range from 3 to 38 mm. of mercury. The average of nine determinations of hydrogen and methane in fraction I gave 21.2 and 78.8%, respectively, with a probable error of 0.8. Combustions of fraction II yielded an aver-

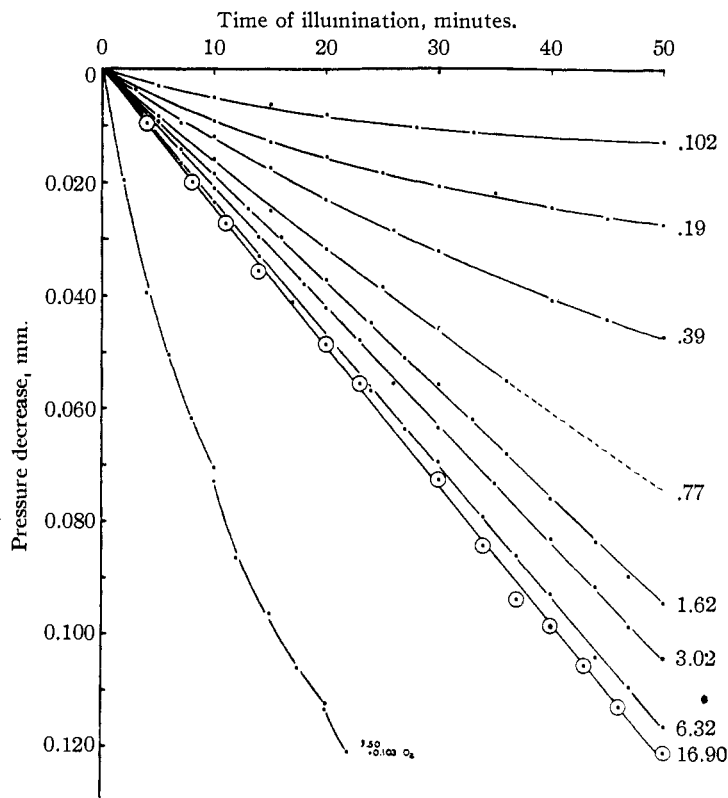


Fig. 2.—Rate of pressure decrease with varying initial pressure.

age number of carbon atoms per molecule of 2.25 with a probable error of 0.07 for four determinations. Two tests of fraction II for unsaturated

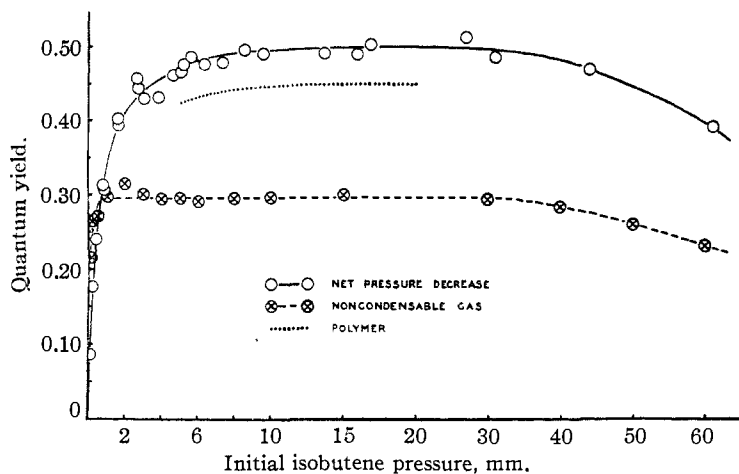


Fig. 3.—Variation of quantum yields with initial pressure.

compounds gave 4.5 and 1.6%, hence the hydrocarbons in this fraction must be chiefly ethane and propane. If any hydrocarbon as heavy as C_4H_n were present, it would certainly be isobutene, and the amount of this compound cannot exceed 5%. Therefore, the composition of fraction II lies between 75% ethane and 25% propane, and 80% ethane, 15% propane and 5% isobutene. The absence of methylacetylene, a product suggested by the results of ethylene photolysis, has already been mentioned. Analyses of fraction III gave an average of 9.05 carbon atoms per molecule.

Using the above data, together with the ratio of fraction I to the net pressure decrease equal to 0.26 and the value of the quantum yield for pressure decrease, the following quantum yields may be calculated: hydrogen, $\phi = 0.03$; methane, $\phi = 0.10$; hydrocarbon averaging 2.25 carbon atoms per molecule, $\phi = 0.16$; polymer averaging 9.05 carbon atoms per molecule, $\phi = 0.45$. These values are applicable in the region of maximum rate.

The number of isobutene molecules necessary to form these products is 1.13 per quantum. On the other hand, the sum of the yields for pressure decrease, non-condensable gas formation, and polymerization requires that at least 1.24 molecules of isobutene disappear per quantum. A carbon balance can be made by assuming molecules containing 5 and 6 carbon atoms to be carried off with isobutene or by the formation of a solid non-volatile polymer. (The

partial pressure of molecules containing 7 or more carbon atoms in such a mixture at -110° is estimated to be below 10^{-4} mm.) It is true that after several runs a white deposit could just be seen on the front window over the area covered by the light beam. Assuming both possibilities to occur, the carbon balance requires

$$n_5 + 2n_6 + n_w = 0.44$$

where n_5 , n_6 and n_w stand for the number of C_5 and C_6 molecules in the gas phase and carbon atoms on the wall per quantum absorbed, respectively. The deposit on the walls

is possibly sufficient to make the balance, since it would require a layer approximately one atom thick. Therefore, it is probable that the number of C_5 and C_6 molecules formed is small.

The effect of light intensity on the rate is shown in Fig. 5. Results obtained by the use of screens are not quite consistent with those in which the intensity of the spark was varied. In the former case, however, uneven illumination could not be avoided. It might be expected that the spectral

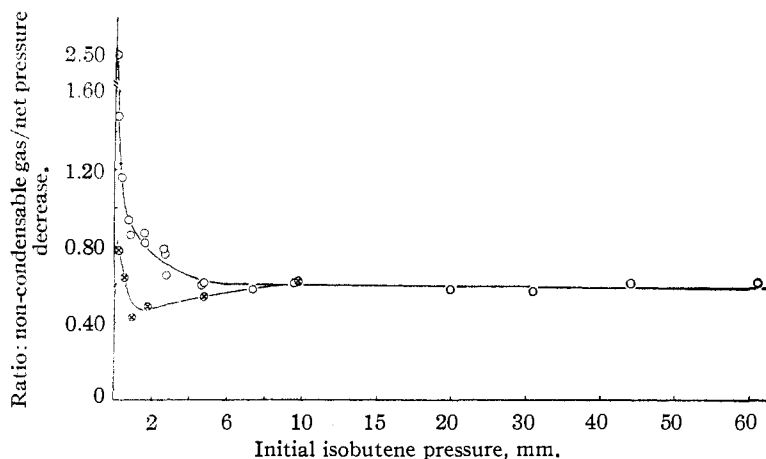


Fig. 4.—Amount of non-condensable gas formed with varying initial pressure: \otimes , lead on cell walls; \circ , cell walls clean.

distribution would be changed in the latter case, but the results are self-consistent enough to warrant the assumption that changes in the relative intensities of the spectral lines may be neglected.

At low pressures the rate deviates markedly from a linear relation with the light intensity.

Added nitrogen had very little effect on the rate, though in the case of a mixture of 7.4 mm. of isobutene and 4.9 mm. of nitrogen the rate was

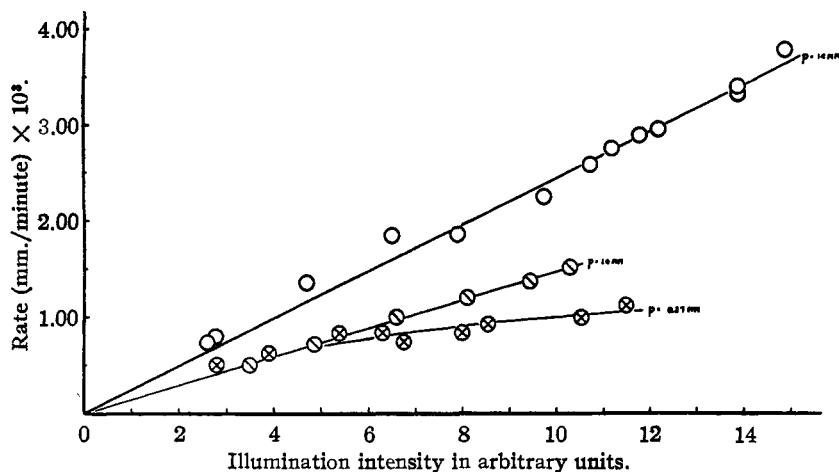
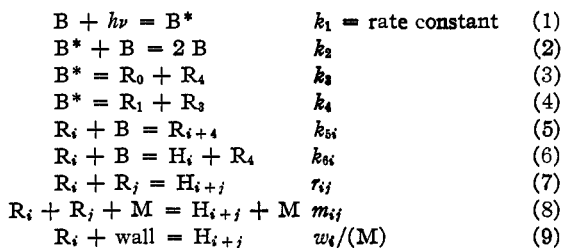


Fig. 5.—Variation of rate with light intensity.

approximately 7% less. In the case of oxygen, the added gas actually enters into the reaction and is used up, apparently altering the reaction considerably.

Discussion

The authors have found it convenient to center the discussion around the following reactions:



Here B and B* represent normal and excited isobutene molecules, respectively. R_i represents a free radical containing i carbon atoms, H_i a hydrocarbon of i carbon atoms consistent with the equation, R_0 is a hydrogen atom, and M is any third body. This is not a completely one to one system of representation but will suffice for this discussion—for instance, there are two R_4 's of different composition C_4H_7 and C_4H_9 and $i \neq 2$, etc.

It seems wise to consider certain broad requirements which the data place on any mechanism before discussing the specific reactions.

From the quantum yields given above, it may be seen that the ratio of isobutene molecules, used for products of fewer carbon atoms than isobutene, to those used for products of more carbon atoms is not greater than 0.113 in this particular pressure range. In the light of this apparent relatively small amount of decomposition it might seem rea-

sonable to assume a mechanism in which an excited molecule may combine with a normal molecule and eventually form a stable dimer. Roughly one in ten excited molecules could break into fragments which could combine in various ways to give the non-condensable gas. However, if this is the only fate of these free radicals or atoms, the rate of all the observed processes would depend linearly on the light intensity at all pressures.

The fact that the rate of pressure change becomes approximately linear in the square root of the light intensity at low pressures as shown in Fig. 6 must require the formation of a relatively large number of free radicals or atoms and a reaction of a fraction of them with isobutene molecules. In addition, one of the reactions involved in maintaining the stationary concentration of the radicals must be a bimolecular combination. Moreover, it is to be noted that the quantum yields, for the formation of non-condensable gas and for net pressure decrease, increase essentially parallelly to one another in the low pressure range. This might indicate that they are connected to a common process. The effect of putting lead on the walls indicates that a large fraction of the free radicals are reaching the walls at pressures below 6 mm.

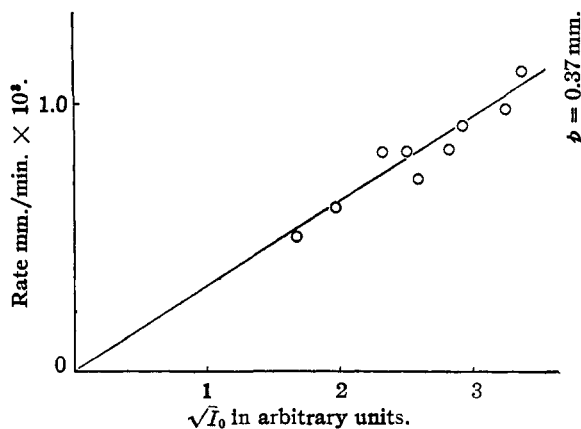


Fig. 6.

The processes of polymerization may best be considered after a discussion of certain primary processes.

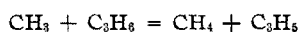
Primary Processes.—The absorption spectrum of the isobutene molecule possesses enough structure to permit, in the case of a complex molecule, the assumption that the primary reaction is reaction (1). The energy absorbed is in excess of that necessary to dissociate any bond in the molecule. Moreover, no fluorescence is observed, hence, in the absence of collisions most of the molecules must dissociate. It would seem highly probable that one type of dissociation would be reaction (4). Although the energy is sufficient to break two carbon-carbon single bonds, it would seem more probable that only one is broken, and that the fragments carry away the excess energy. Reaction (3) accounts very simply for the production of hydrogen. Secondly, it would be consistent with the notion presented by Taylor¹⁰ that a radical of the type $\text{H}_2\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$ would be stabilized by resonance, and hence that the potential energy surface for a molecule such as propene or isobutene would possess a relatively low pass for the removal of an H atom.

Another possible reaction in view of the complexity of the molecule is



B_2^* possesses so much energy it must be short-lived, perhaps dissociating within a few vibration periods. It may be considered an intermediate stage in reaction (2). Stabilization of B_2^* would require the shift of a hydrogen atom or a methyl group from one carbon to another. While this process does take place in a condensed phase, and hence probably on the wall, it must be rather improbable in the gas phase. It might be important at high pressures where the light absorption occurs in a layer very close to the wall and the slight amount of polymerization which occurs appears to take place on the walls.

Reactions Producing Molecules Larger than Isobutene.—Although eq. (2') cannot be ruled out by the data, it can be shown to be unnecessary in the present work if it is assumed that reactions (5) through (8) are possible. Smith and Taylor¹⁰ have found that the reaction



has an activation energy of 3 kcal., hence at least 0.0067 of the collisions between methyl groups and isobutene at 25° have energy enough for (6). Re-

actions of the type (5) have been postulated in many cases.^{6j}

Bimolecular reactions of the type (7) and (8) should be highly probable in the gas phase for free radicals of such complexity and unquestionably proceed on the wall of the cell. If (6) were the only fate of the primary radicals, R_4 could react only with itself to give a diene containing 8C atoms. Disproportionation¹¹ in this case would lead to isobutene and a radical which could be stabilized only by complete rearrangement of the carbon atoms, though it might be comparatively stable itself due to resonance. At best, however, (6) and (7) must produce at least two light molecules for every heavy one. The data in Fig. 4, then, require some other process, such as (5), in the region of maximum rate.

A great deal more speculation is possible, but the number of reactions included in (5), (6), (7), (8) and (9) is already so great as to make arguments somewhat diffuse. The possibility of splitting the carbon-carbon double bond is allowed energetically, but would require an entirely unfamiliar series of reactions subsequently.

Deductions from the Mechanism.—The authors have inspected the steady-state equations for reactions (1) through (9) by means of two methods of approximation. However, since no evaluation of rate constants is possible, only the general results are mentioned here very briefly. It may be shown that the rate of pressure decrease

$$\frac{dp}{dt} = (\text{B}) \sum_i k_{si}(\text{R}_i)$$

where the parentheses denote concentrations. It is possible to expand (R_i) in a power series in (B^*) which will converge when $k_1 h \nu$ is sufficiently small and/or (B) sufficiently large. In the region where the rate is linear in light intensity, the first term of the expansion is sufficient and if no foreign gas is present, leads to an expression for the quantum yield for pressure decrease of the form

$$\phi = \frac{(\text{B})^2}{k_2 + k_4 + k_2(\text{B})} \text{Q}$$

where Q is a ratio of a polynomial in $(\text{B})^2$ of order $[n(n+1)/2] - 1$ to one of order $n(n+1)/2$ where $4n$ equals the total number of free radicals. The coefficients in the polynomials involve the k_s 's, k_6 's and w 's and are all positive. It can be seen that such an expression behaves in a similar fashion to the plot of ϕ against p in Fig. 3.

(10) Hugh S. Taylor, paper given before the New York Academy of Sciences Conference on Photochemistry May 3 and 4, 1940; J. O. Smith and H. S. Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

(11) Jungers and Taylor, *ibid.*, **6**, 325 (1938).

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.

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[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).