

## The Mercury Photosensitized Reactions of Isobutene

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## The Mercury Photosensitized Reactions of Isobutene\*†

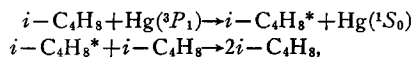
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(Received July 1, 1948)

An investigation has been made of the reaction of isobutene with mercury ( $^3P_1$ ) atoms at 30°C. Acetylene and propylene have been shown not to be among the main products of the reaction. The over-all rate of consumption of isobutene and the rate of pressure decrease both decrease with increasing initial pressure in the complete quenching region. These rates approach constant values for initial pressures of 180 mm and higher. The results of this investigation show that isobutene behaves similarly to the other olefins in reacting with mercury ( $^3P_1$ ) atoms at 30°C, in that the reactions can be explained by the following initial steps

for the mechanism:



accompanied by the decomposition of the activated isobutene molecule into reaction-initiating fragments.

The discrepancies between the results of this investigation and those of the earlier work of Gunning and Steacie may be due to the effect of impurities in the original isobutene, since it is shown that small amounts of added propylene or acetylene change the rate of reaction markedly.

## INTRODUCTION

IT has been shown that ethylene,<sup>1</sup> butadiene,<sup>2</sup> propylene,<sup>3</sup> isoprene,<sup>3</sup> 1-butene,<sup>4</sup> and 2-butene<sup>4</sup> all react with mercury ( $^3P_1$ ) atoms, at room temperature, by an activated molecule mechanism. Isobutene,<sup>5</sup> however, seemed to be inconsistent with the other olefins in this respect, since no rate-decreasing deactivation was detected at initial isobutene pressures up to 84 mm, thus permitting a mechanism postulating an initial split into  $C_4H_7$  radicals and H atoms. However, this point was not firmly established, since pressures of the order of 80 mm, measured on the McLeod gauge used, would have a low degree of accuracy, and the rates determined in the isobutene investigation would be no more accurate than the pressure measurements.

In order to find out more about this apparent difference between the reaction mechanism of

isobutene and that of the other olefins, the investigation of the isobutene reaction was repeated and extended to higher pressures, using a more accurate method of determining pressure changes.

## EXPERIMENTAL

## Static Runs

Static runs were made using a cylindrical quartz cell, 10 cm in length, with windows 5 cm in diameter. Its volume was about 190 ml. The cell was immersed in a metal water bath provided with a fused quartz window. The distilled water in the bath was kept at  $30.00 \pm 0.01^\circ\text{C}$  by means of a thermoregulating system consisting of a mercury thermoregulator, an immersion heater, and a thermionic relay as described by Serfass.<sup>6</sup> The cell was connected to the rest of the reaction system by means of a standard taper ground-glass joint. The reaction system, comprising the cell, a small finger trap for freezing out condensable materials, and an automatic Pearson type differential manometer,<sup>7</sup> had a zero pressure volume of 280 ml. (The volume, being dependent on the mercury level in the differential manometer, varied with the pressure in the system; since the manometer tube was calibrated, the volume for any given setting of the mercury level could easily be determined.)

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† Part of a dissertation submitted by one of the authors (G. A. A.) in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Rochester.

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<sup>1</sup> D. J. LeRoy and E. W. R. Steacie, *J. Chem. Phys.* **9**, 829 (1941).

<sup>2</sup> H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **12**, 484 (1944).

<sup>3</sup> H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 57 (1946).

<sup>4</sup> H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 581 (1946).

<sup>5</sup> H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.* **14**, 544 (1946).

<sup>6</sup> E. J. Serfass, *Ind. Eng. Chem., Anal. Ed.* **13**, 262 (1941).

<sup>7</sup> D. J. LeRoy, *Ind. Eng. Chem., Anal. Ed.* **17**, 652 (1945).

All rates reported refer to the base volume of 280 ml.

The presence of mercury vapor in the reaction cell was ensured by having a pool of mercury in a 1 ml well in the bottom of the cell. After each run, the cell was removed at the standard taper joint, cleaned with chromic acid cleaning solution, and flamed to ensure the removal of any residual polymer. Fresh mercury was placed in the well before reconnecting the cell to the system; fresh Apiezon stopcock grease "N" was used on the standard taper joint each time that the cell was reconnected.

Water was circulated through a water jacket surrounding the differential manometer and through a copper coil immersed in the water bath in order to maintain both the reactant in the manometer part of the cell system and the mercury of the manometer at a constant temperature of approximately 30.0°C.

The reaction system was connected by a mercury-operated glass float-valve cut-off to another separable system which included a McLeod gauge. This system in turn was connected by a similar mercury cut-off having glass check-valves to the main manifold, to which were attached gas reservoirs, a double-trap distillation purification apparatus, sampling devices, and the pumping system.

A Hanovia Sc2537 mercury resonance lamp, in the form of a spiral 5 cm in diameter and 10 cm long was clamped firmly broadside on to the quartz window of the water bath, the coils nearest the window being 20 mm from the window. The lamp was enclosed on all sides except that facing the window by a wooden box shield, the interior of which was painted dull black; the shield prevented external draughts from affecting the operation of the lamp, and from changing the concentration of ozone produced by  $\lambda 1849$  line between the lamp and the bath.

The lamp was operated for at least one hour prior to each run, in order to attain equilibrium operating conditions. A thin sheet of metal, placed between the bath and the lamp, served as a removable shutter. The lamp was operated from the secondary of a Jefferson 6000 volt 120 milliampere sign transformer. A.c. line voltage variations of 10 volts were found to affect the rate

TABLE I. Analyses of original isobutene.

Component	Sample 1, mole percent	Sample 2, mole percent	Average, mole percent
Propylene	1.5	1.5	1.5
Isobutane	1.0	1.0	1.0
<i>n</i> -Butane	0.6	0.5	0.55
Isobutene	96.8	96.9	96.85
Butadiene	0.1	0.0	0.05

of pressure change by about 15 percent; therefore the transformer primary was fed 110 volts from a Variac, this input voltage being checked at 5- or 10-minute intervals throughout the course of each run. Normal operating characteristics of the lamp were: lamp current,  $100 \pm 5$  ma, lamp voltage  $570 \pm 15$  volts.

The isobutene used in the experiments was obtained from the Matheson Company, East Rutherford, New Jersey, and was stated to be at least 95 percent isobutene. It was further purified by several trap-to-trap distillations, only the middle fraction of each distillation being retained, and was finally stored in a storage flask. The storage flask was connected to the manifold of the system, through a mercury cut-off having glass check valves and also through a modified stock valve as designed by Warrick and Fugassi.<sup>8</sup> Table I gives the mass spectrometric analyses of duplicate samples of purified isobutene.

The propylene used was obtained from the same source, purified in the same manner, and stored in a storage flask which was connected to the manifold by means of a modified stock valve identical to the one used for the isobutene. The acetylene used was commercial grade, and was obtained from the Air Reduction Company. It was purified by several trap-to-trap distillations immediately prior to using.

The nitric oxide used in this work was prepared by the action of mercury on a 2 percent solution of sodium nitrite in concentrated sulfuric acid.<sup>9</sup> It was then purified by several trap-to-trap distillations, from dry ice-acetone bath temperature ( $-78.5^\circ\text{C}$ ) to liquid nitrogen temperature.

To determine whether the surface of the cell

<sup>8</sup> E. Warrick and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.* **15**, 13 (1943).

<sup>9</sup> A. Klemenc, *Die Behandlung und Reindarstellung von Gasen*, p. 166, (Akademische Verlagsgesellschaft b. Leipzig, 1938).

had any great effect on the rate of pressure decrease, one run was made in which the interior surface of the cell was coated with potassium chloride. The coating was obtained by rinsing the cell with a saturated solution of potassium chloride in alcohol and water, then drying the cell before adding mercury to the cell well and reconnecting the cell to the reaction system.

### Single Pass Runs

Two single pass runs were made to make qualitative observations on products. In each of these runs, a few ml of liquid isobutene were distilled from a trap reservoir immersed in dry ice-acetone, passing through a quartz reaction tube 10 mm in diameter to a receiver immersed in liquid nitrogen. The vapor pressure of isobutene at dry ice-acetone temperature is about 10 mm; hence the pressure of the isobutene should be that corresponding approximately to maximum rate of pressure decrease. The isobutene, on leaving the reservoir, was bubbled through or passed over the surface of a pool of mercury at room temperature, to ensure the presence of mercury vapor in the reaction tube. A helical mercury resonance lamp identical with the one used for static runs, was placed coaxially about the quartz section of the reaction tube.

### Analytical Methods

After each run, a Dewar flask of liquid nitrogen was placed around the finger trap of the reaction system. When the condensable products and unreacted isobutene were completely frozen out, the cut-off between the reaction system and the McLeod gauge was opened, and the pressure of

the non-condensable gas was measured. (Experience showed that it could be assumed that all the condensable substances were completely frozen out within 10 to 20 minutes after the liquid nitrogen was placed around the finger trap.) Gunning and Steacie<sup>6</sup> reported the rates of formation of hydrogen and methane in the reaction; since these were minor products, with very low rates of formation, and since the rate of formation of total non-condensables found in the present investigation agreed reasonably well with the rates of formation of hydrogen plus methane reported by Gunning and Steacie, the non-condensable gas was not analyzed further.

In a number of runs, acetylene was then sought in the mixture of reaction products by the method of Ross and Trumbull,<sup>10</sup> as modified by LeRoy and Steacie.<sup>1</sup>

An attempt was made to determine propylene in the reaction products by means of infra-red spectrometry, but it was found impossible to detect low percentages of propylene in the presence of high percentages (about 80–95 per cent) of isobutene.

In order to determine the amount of propylene formed, and to investigate what other products were being formed, arrangements were made with Dr. W. H. Barcus, Manager of the Development Laboratory, Sun Oil Company, to have analyses of the products of several runs covering a wide pressure range performed on the mass spectrometer. In each of these runs, after the gas non-condensable in liquid nitrogen had been determined, the entire condensable portion of the reaction mixture was frozen out into an evacuated sample bulb attached to the main manifold. When the McLeod gauge showed that the pressure in the system had fallen to a constant value approximately equal to the pressure of the non-condensable gases dispersed throughout the combination of the reaction cell, McLeod gauge, and manifold, the sample bulb was sealed off and removed from the system.

### Actinometry

The intensity of the light entering the cell was determined by the uranyl oxalate-oxalic acid

TABLE II.

Run No.	$P_0$ mm	$-\Delta P/\Delta t$ mm/min. $\times 10^2$	Run No.	$P_0$ mm	$-\Delta P/\Delta t$ mm/min. $\times 10^2$
62	1.08	1.88	50	50	1.57
61	3.65	2.21	47	52.5	1.59
59	7.5	2.28	49	55	1.53
66	10.2	2.09	48	58	1.65
69	12.1	2.0	54	84	1.26
75	12.5	2.01	52	110	0.90
55	13.8	2.14	56	158	0.84
53	23	1.84	57	183	0.76
74	24	1.88	73	240	0.73
58	38	1.43			

<sup>10</sup> W. H. Ross and H. L. Trumbull, *J. Am. Chem. Soc.* **41**, 1180 (1919).

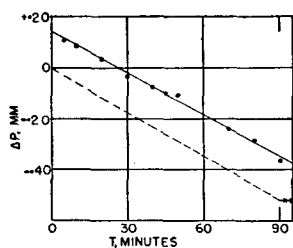


FIG. 1. Pressure decrease vs. time for a static run (initial pressure 240 mm), showing the initial pressure rise and the corresponding "dark" pressure decrease when the lamp was turned off at  $t=90$  minutes.

method.<sup>11,12,13</sup> The uranyl oxalate was precipitated from a saturated aqueous solution of C.P. uranyl nitrate by the addition of an alcoholic solution of C.P. oxalic acid, washed with alcohol, filtered, dried overnight in a desiccator, and finally dried at 110°C for 3 hours. The actinometry solution was made up approximately 0.001 N in uranyl oxalate and 0.005 N in oxalic acid, and was stored in a light-tight glass bottle. Potassium permanganate solution was made up and its normality determined as 0.0164 N by standardization against C.P. grade sodium oxalate.

For the actinometric runs, 200 ml of uranyl oxalate-oxalic acid solution was pipetted into the reaction cell. The cell was then reconnected to the reaction system, and illuminated for a measured time, the lamp first having been operated for at least an hour in order to ensure equilibrium operating conditions of the lamp. Ten ml concentrated sulfuric acid were added to duplicate 50 ml aliquot portions of the photolyzed solution, which were then titrated at 80–85°C with standard potassium permanganate solution. The oxalate concentration of the original actinometry solution was similarly determined, using duplicate 50 ml portions.

### RESULTS

For initial isobutene pressures less than about 10 mm, the plot of pressure decrease against time was a straight line passing through the origin. In the case of initial pressures greater

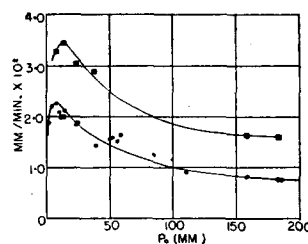


FIG. 2. ■ Rate of consumption of isobutene vs. initial pressure. ● Rate of pressure decrease vs. initial pressure. (Both rates in mm/minute  $\times 10^2$  for a volume of 280 ml.)

than about 10 mm, an apparent induction period was observed; this apparent induction period was greater the greater the initial pressure, and ranged from 1 to 25 minutes. At higher pressures, a slight initial pressure rise was observable during this period, thus indicating that the apparent induction period was actually due to a pressure rise occurring during the first two minutes of the reaction. Extrapolation of the linear pressure decrease-time curve to zero time produced a positive  $\Delta P$  intercept ranging from 0.01 to 0.15 mm, being greatest for greatest initial pressures. Moreover, when the lamp was shuttered at the end of a run, the pressure dropped by an amount approximately equal to the pressure rise intercept. These observations are clearly seen in Fig. 1.

The rates of pressure decrease are given in Table II; Fig. 2 shows these data in graphical form.

### Products

The rate of disappearance of isobutene and the rates of formation of products, calculated from the pressure rates and the mass spectrometric analyses, are reported for a number of runs in Table III. The rate data reported for the two lowest pressures are not very reliable, since the reactions were carried out to a high percentage decomposition (71 percent and 50 percent for initial pressures of 1.08 and 3.65, respectively). It should be pointed out that the presence of neopentane in the reaction products is uncertain, since no pattern for pure neopentane had been run on the mass spectrometer; it may be that heptanes, octanes, heptenes, and octenes were present, giving rise to lower mass peaks similar to neopentane. Analytical results were calculated on the basis of neopentane, which

<sup>11</sup> W. G. Leighton and G. S. Forbes, J. Am. Chem. Soc. 52, 3139 (1930).

<sup>12</sup> F. P. Brackett, Jr. and G. S. Forbes, J. Am. Chem. Soc. 55, 4459 (1933).

<sup>13</sup> G. S. Forbes and L. J. Heidt, J. Am. Chem. Soc. 56, 2363 (1934).

TABLE III. Rates of formation.

Initial pressure (mm)	1.08	3.65	7.5	13.8	23	38	110	158	183
Component:	(All rates in moles per minute $\times 10^8$ )								
isobutene	-51.9	-51.7	-48.6	-51.1	-45.2	-42.7	(-51.3)	-24.3	-23.7
<i>n</i> -butane	8.5	4.3	2.6	7.5	10.8	8.1	(31.6)	2.3	8.4
isobutane	1.9	5.9	8.3	4.1	0.85	0.73	0.16	0.13	0.1
pentenes	3.6	1.9	1.4	2.2	1.7	1.9			
neopentane	5.5	2.9	1.8	5.0	5.6	5.8			
propylene	-1.1	-0.8	-1.1	-0.8	-1.0	1.6	-0.2	9.3	5.5
butadiene	0.33	0.15	0.06	0.46	0.81	1.43	1.56	2.4	2.8
ethane	2.8	0.07							
propane	0.45								
isopentane	0.9	0.28							

would cause the maximum errors in analysis to be in the percentage of propylene and isobutene. An error of 0.1 to 0.2 percent in the propylene analyses at higher pressures would reverse the sign of the reported rates of formation.

Analysis of the products of each of several preliminary one-hour static runs for acetylene by the method of Ross and Trumbull<sup>10,1</sup> indicated less than 4 micromoles of acetylene present. (The reagent blank was of the order of 1.5 micromoles.) No acetylene could be detected by mass spectrometric analysis; assuming that this method could detect 0.1 mole percent, an upper limit of 0.01 micromoles per minute may be given for the rate of production of acetylene.

#### Products of Single Pass Runs

A viscous polymer which seemed to yellow with continued irradiation was observed on the walls of the reaction tube. The polymer was soluble in benzene and in petroleum ether. Non-condensable gas was formed at a rate of about 0.2 micromoles per minute. After pumping off the gas non-condensable in liquid nitrogen, the bulk of the residual isobutene was distilled off at dry ice-acetone temperature. About 1-2 ml of a

liquid product remained in the still at dry ice-acetone temperatures. This liquid had a vapor pressure of 0.03 mm at  $-78^\circ\text{C}$ , 22 mm at  $0.0^\circ\text{C}$ , and 62 mm at  $25^\circ\text{C}$ .

#### Effect of Added Impurities

Several runs were made with small amounts of added nitric oxide, propylene, or acetylene. In all cases, except one, the initial rates of pressure decrease were greater than the rates for the same partial pressure of isobutene without added impurities, as shown in Table IV. With added propylene or acetylene, the pressure decrease was entirely linear with time. However, in the runs with added nitric oxide, the rate of pressure decrease finally decreased to a value approximately the same as that for pure isobutene at the same partial pressure, as shown in Fig. 3. The length of time elapsing before the rate decrease occurred varied with the amount of nitric oxide initially added. Furthermore, the pressure of non-condensable gas measured at the end of the nitric oxide runs was always less than the vapor pressure of nitric oxide at liquid nitrogen temperatures, indicating that the bulk of the nitric oxide was used up during the reaction.

TABLE IV.

Run No.	Partial pressure of isobutene	Compound added	$-dP/dt$ mm/min. $\times 10^2$	% change in rate
67	10.3	Nitric oxide, 11%	9	350
68	11.3	Nitric oxide, 1.2%	10	400
71	11	Nitric oxide, 0.91%	3.6	70
77	9.8	Nitric oxide, 0.14%	2.2	0
76	8.7	Propylene, 7.3%	2.82	26
85	21	Acetylene, 5.5%	4.24	120
86	20	Acetylene, 1.5%	2.25	16

#### Light Intensity and Quantum Yield

The results of the uranyl oxalate-oxalic acid actinometric determinations are reported in Table V. Note the agreement between runs  $A_1$  and  $A_2$ , in which the percentages decomposition of oxalate ion were 13 and 50 percent, respectively. Runs  $A_3$  and  $A_4$  were made after repairs to the reaction system had been made between runs 77 and 79. Run  $A_5$  served to calibrate

a sulfidized copper gauze placed between the lamp and the reaction cell.

With the sulfidized copper gauze in place reducing the light intensity to 0.30 of its unreduced value, the results tabulated in Table VI were obtained. (Values of normal rates were obtained from Fig. 2 by interpolation, when necessary.)

The quantum yield of isobutene consumption, calculated from the data of Tables III and V, is of the order of 0.03.

One one-hour run was made in which the lamp was shuttered for 1 minute after each 10 minutes of exposure. The pressure increased slightly each time that the cell was exposed to the light, and decreased immediately after each shuttering of the lamp. Neglecting these phenomena, the graph of pressure decrease against time of exposure was linear, and the rate of pressure decrease determined from the graph was the same as that for a normal continuous-exposure run made at the same initial pressure.

### Effect of Surface

The rate of pressure decrease measured for an initial pressure of about 10 mm when the cell was coated with potassium chloride was about 5 percent lower than the rate observed for the same initial pressure in the uncoated cell.

### DISCUSSION

The decrease in rate of consumption of isobutene with increasing initial pressure, paralleled by the decrease in rate of pressure decrease, can best be explained by postulating the formation of an activated isobutene molecule as the product of the initial quenching process. On this basis the initial steps would be the following:

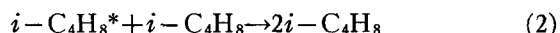
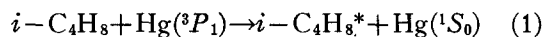


TABLE V.

Run No.	Percent decomposition	Intensity einsteins/min. $\times 10^6$
A <sub>1</sub>	13	1.6
A <sub>2</sub>	50	1.59
A <sub>3</sub>	50	1.64
A <sub>4</sub>	53	1.70
A <sub>5</sub>	32	0.51

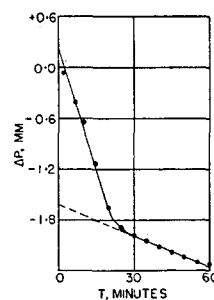
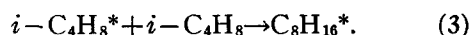


FIG. 3. Pressure decrease vs. time for a static run with 1.3 vol. percent of nitric oxide. (Initial isobutene pressure 11 mm.)

with  $i-C_4H_8^*$  leading to reaction if not deactivated.

Both the rate of isobutene consumption and the rate of pressure decrease appear to approach a constant value for initial pressures of the order of 180 mm and higher. Furthermore, in this initial pressure region, the ratio of these respective rates is approximately 2. This suggests that the chief reaction in this region of complete deactivation is dimerization, i.e., that simultaneous with reaction (2) there is a reaction of the type



While the dimer thus formed would be "hot," its large number of degrees of freedom should permit it a long enough life that the excess energy would be removed by collisions. The presence among the single-pass products of a liquid in the  $C_7$ – $C_8$  vapor pressure range certainly tends to support the suggestion of dimer formation. However, establishment of this proposed dimerization step and postulation of other steps of the mechanism must await the results of the investigation now being initiated using purer initial reactant, in which more accurate analytical data on the reaction products, including up to the  $C_8$  fraction, will be sought.

TABLE VI.

Run No.	$P_0$ mm	$-dP/dt$ mm/min. $\times 10^2$	Rate at reduced intensity Rate at full intensity
83	8.1	0.70	0.31
81	11.7	0.69	0.32
79	11.7	0.78	0.36
82	29.5	0.495	0.27
80	57	0.399	0.26

The absence of acetylene from the major products found in this observation suggests that in Gunning and Steacie's investigation,<sup>8</sup> either an acetylene-generating impurity was present, or acetylene itself was present as an undetected impurity. Their rate of pressure decrease, reduced to a system volume of 280 ml, was about three times that observed in the present investigation, whereas their light intensity, based on the mercury photosensitized reactions of ethylene and corrected in accordance with recent data on the ethylene reaction,<sup>14</sup> was 0.55 times the intensity used in the present investigation. Assuming the rate of pressure decrease to be directly proportional to light intensity, Gunning and Steacie's observed rate was greater than that found by the authors by a factor of 5.5. Results of the present investigation show that added acetylene increases the observed rate of pressure decrease (see Table IV), which supports the suggestion that acetylene may have been present as an impurity in the original gas used by Gunning and Steacie.

The increase in rate when propylene is added to the reacting isobutene indicates that the rates determined by Gunning and Steacie<sup>5</sup> and by the authors may be inaccurate, since propylene was present in the original isobutene to the extent of 1 percent and 1.5 percent, respectively. An investigation using much purer isobutene is under way in these laboratories.

The increase in reaction rate in the presence of added nitric oxide, together with the consumption of the nitric oxide in the course of the reaction, suggests that a mercury photosensitized reaction of nitric oxide with isobutene occurs, similar to that suggested in the case of butadiene.<sup>2</sup>

For our purpose, therefore, these results are irrelevant.

The identification of the apparent induction period with a real pressure increase very closely equal to the pressure decrease observed on shuttering the lamp suggests that these phenomena are due to some physical cause similar to the Budde effect<sup>15</sup> and the Draper effect.<sup>16</sup>

### CONCLUSIONS

The results of the present investigation show that isobutene forms an activated molecule in the initial quenching process, although simultaneous alternative processes cannot be eliminated on the basis of these results. Nevertheless isobutene has now been shown to quench in an analogous manner to the other olefins which have been previously investigated—ethylene,<sup>1</sup> butadiene,<sup>2</sup> propylene,<sup>3</sup> isoprene,<sup>3</sup> 1-butene,<sup>4</sup> and 2-butene.<sup>4</sup>

Proposal of a detailed mechanism for the reaction must await investigation of the reaction using a purer initial reactant than heretofore and more accurate analyses of the products formed. Such an investigation might also conceivably shed some light on the low value of quantum yield found in the present investigation.

### ACKNOWLEDGMENTS

It is a great pleasure to acknowledge our indebtedness to the Sun Oil Company and to Dr. W. H. Barcus of their Development Laboratory for their kindness in performing the mass spectrometric analyses reported in this paper.

Our thanks are also extended to Mr. Burton E. Dearing for his assistance in making infra-red absorption measurements.

<sup>14</sup> G. A. Allen and H. E. Gunning, *J. Chem. Phys.* **16**, 634 (1948).

<sup>15</sup> E. Budde, *J. prakt. Chem.* **7**, 376 (1873).

<sup>16</sup> J. Draper, *Phil. Mag.* **26**, 476 (1845).