

the interior of the isothermal, composition-pressure hysteresis loops exhibited by this system. The effect was not always observed and depended somewhat on the region of the loop under investigation. The effect, when evident, was most noticeable near the center of the hysteresis envelopes.

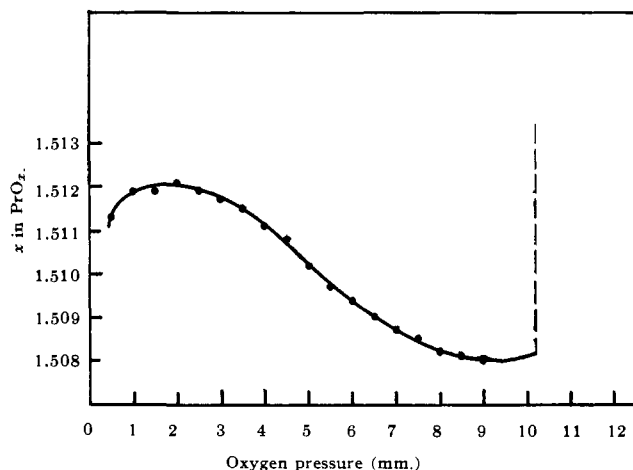


Fig. 1.—The variation of composition with oxygen pressure at 900°

(2) A related effect was also noted during the study of the phase diagram of the Pr-O system.<sup>5</sup> A typical high temperature (>900°) isothermal uptake, from fairly low pressures up to a "break" pressure where rapid uptake occurred, is illustrated in Fig. 1. The effect was not observed below 900°. The data for the curve were taken over a period of 5 days. It can be seen from the figure that as the oxygen pressure was increased at constant temperature, the amount of gas taken up at first increased, then became relatively constant, and finally decreased slightly. Upon a further pressure increase the uptake again increased slightly until a critical pressure was attained, at which value the uptake cascaded. The cascade reaction is probably related to the surface reaction in an isotheric way. The region of interest here is the pressure region for pressures less than the cascade pressure.

(3) In addition to these two irregularities, another peculiar pressure effect has been observed during a study of the rate of uptake of oxygen by hexagonal Pr<sub>2</sub>O<sub>3</sub>.<sup>6</sup> It was found that while the rate of bulk uptake increased rapidly with increasing pressure as expected, the amount initially taken up (rapid initial adsorption) prior to bulk uptake appeared to be inversely proportional to the ambient pressure. Slightly more gas was taken up initially by the surface at lower oxygen pressures than at higher pressures. The pressure range observed was between 9 and 23 torr oxygen and the gas had been admitted as rapidly as possible. The results of these latter studies are in preparation and will be reported shortly.

At high temperatures the temperature dependence of the PrO<sub>x</sub>-O<sub>2</sub> system is such that the uptake increases with decreasing temperature. Some uptake could be accounted for by considering a lowering of the solid

temperature during the rapid admissions of oxygen. However, a pressure effect opposite to that observed would be expected. From the three observations of O<sub>2</sub> on PrO<sub>x</sub> noted above, one might conclude that the initial rapid adsorption involves some kind of a reflex action at the surface. Additional work is planned to help elucidate these findings.

**Acknowledgment.**—This work was sponsored in part by the U. S. Air Force under contract AF 18(603)-45.

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RECEIVED MARCH 4, 1964

### The Initiation of Ionic Reactions in Liquid Hydrocarbons via Photoionization with Vacuum Ultraviolet Radiation. The Polymerization of Isobutylene

Sir:

We wish to report a novel method for studying ionic reactions in low dielectric liquids which does not depend upon the presence of a chemical initiator or a stabilizing surface to sustain the reaction.

A study of the ionic polymerization of isobutylene is a particularly good test case since the ionic nature of this reaction at low temperatures appears well established and there is little interference from free-radical processes. Such ionic polymerizations are usually chemically initiated by a catalyst-cocatalyst system interacting with reactants in an active solvent medium.<sup>1</sup> It is obviously quite difficult to assess the importance of the individual components in such a multicomponent system. Another method of approach was attempted by Davison, Pinner, and Worrall in the  $\gamma$ -ray polymerization of isobutene at low temperatures,<sup>2</sup> where there is strong evidence for an ionic mechanism. Several other  $\gamma$ -ray-induced polymerizations have also been claimed to go by an ionic process,<sup>3</sup> though this has often been difficult to establish. It has, however, been found that the presence of various solids, including powdered glass, considerably enhances the polymerization yields of such reactions<sup>4</sup> and, hence, makes it likely that the heterogeneous surface is necessary for the polymerization process. In the absence of an added solid, the vessel walls serve to provide the heterogeneous surface. Though the initial process is probably the ejection of an electron, this will recombine

(1) See, e.g., W. C. J. de Loecker, *Ind. Chim. Belge*, **24**, 238 (1959).

(2) (a) W. H. T. Davison, S. H. Pinner, and R. Worrall, *Chem. Ind. (London)*, 1274 (1957); (b) W. H. T. Davison, S. H. Pinner, and R. Worrall, *Proc. Roy. Soc. (London)*, **A252**, 187 (1959).

(3) For a partial list, cf.: (a) A. Charlesby, "Atomic Radiation and Polymers," Pergamon Press, New York, N. Y., 1960, p. 389; (b) M. Magat, *Makromol. Chem.*, **35**, 159 (1960); (c) E. Collinson, F. S. Dainton, and H. A. Gillis, *J. Phys. Chem.*, **63**, 909 (1959); (d) A. Charlesby and J. Morris, *Proc. Roy. Soc. (London)*, **A273**, 387 (1963); (e) T. H. Bates, *Nature*, **197**, 1101 (1963); (f) C. David, F. Provoost, and G. Verduyn, *Polymer*, **4**, 391 (1963); (g) J. V. F. Best, T. H. Bates, and T. F. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962); (h) W. S. Anderson, *J. Phys. Chem.*, **63**, 765 (1959); (i) A. Chapiro and V. Stannett, *J. Chim. Phys.*, **56**, 830 (1959).

(4) (a) R. Worrall and S. H. Pinner, *J. Polymer Sci.*, **34**, 229 (1959); (b) R. Worrall and A. Charlesby, *Intern. J. Appl. Radiation Isotopes*, **4**, 84 (1958); (c) F. L. Dalton and K. Hayakawa, *Polymer*, **4**, 285 (1963); (d) A. Charlesby, S. H. Pinner, and R. Worrall, *Proc. Roy. Soc. (London)*, **A259**, 386 (1960).

(5) J. M. Honig, A. F. Clifford, and P. A. Faeth, *Inorg. Chem.*, **2**, 791 (1963).

(6) P. A. Faeth and A. F. Clifford, "Rare Earth Research," K. Vorres, Ed., Gordon and Breach, New York, N. Y., in press.

with the cation in a time too short to allow for polymerization in the absence of a solid acting as a stabilizing agent for the conjugate electron.<sup>3c</sup>

The study reported here differs from the above experiments in that (a) the initial species are produced by the irradiation (vacuum ultraviolet) of pure isobutylene, and (b) polymerization is carried out in the presence of an applied electric field. The first part ensures that one is dealing with known initial species produced in the vapor phase by well-studied ion-molecule reactions and the second is designed to eliminate the need for an added gegenion or a heterogeneous surface for the polymerization process.

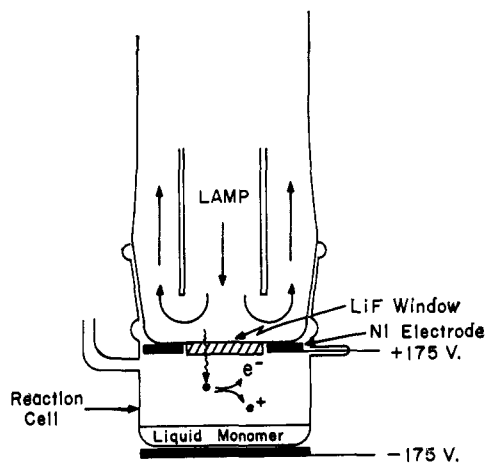


Figure 1.

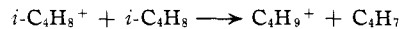
A modified high intensity resonance light source ( $\sim 10^{16}$  quanta/sec.) emitting the krypton lines (1165 and 1236 Å.) was employed for this process. This energy is sufficient to produce photoionization in isobutylene.<sup>5</sup> The details of the light source were reported previously.<sup>6</sup> Various designs for the placement of the electric field were investigated. One electrode was always near the window of the light source (as shown in Fig. 1), and the other on the bottom of the reaction vessel below some liquefied monomer. The only successful experiments were those in which the cathode is placed on the outside of the reaction vessel, below the liquid monomer (see Fig. 1). Placing the cathode on the inside produced no measurable yield. Similarly, runs with reversed polarity produced no polymer, whereas reversing again to the proper polarity gave an immediate visual formation of polymer. The yield (ca. 0.2 g. in 1 hr.) and molecular weights (ca. 1-4 million) were approximately independent of the applied voltage from 90 to 900 v. A photoionization cell of dimensions similar to the reaction cell and filled with pure gas at the same pressure showed that 90 v. was still on the linear portion of a voltage-current plot, hence indicating that this pressure adequately quenches any multiplication processes. The reaction vessel was stirred and kept carefully at the selected temperature between  $-115$  and  $-145^\circ$  with a low temperature thermostat. For a twofold increase in intensity the yield increased by over a factor of three, whereas the molecular weight showed essentially no change. Increasing

(5) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectr. Radiative Transfer*, **2**, 369 (1962).

(6) E. W. Schlag and F. J. Comes, *J. Opt. Soc. Am.*, **50**, 866 (1960).

the surface by the addition of glass wool had no effect on yield or molecular weight.

The conclusions from the above would be consistent with an ion-molecule reaction in the liquid phase initiated by *t*-butyl carbonium ions from the gas phase. These carbonium ions are formed by hydrogen abstraction, such as has been observed at higher pressures in the mass spectrometer.<sup>7</sup> The rate of initiation at these



light intensities appears to be controlled by the rate of production of primary ions by the light source. Much higher intensities appear to be required to saturate the electrodes with as many initiating carbonium ions as could be stabilized by the applied field. The external cathode most likely serves to prevent annihilation of the ion at the electrode which would thus lower the concentration of initiating species. The eventual chain length may be determined by precipitation rather than by the time necessary for the polymer to find an electron, in which case the polymer might be "live." Perhaps most important, the absence of surface effects in this polymerization leads one to conclude that this may well be a case of a homogeneous ionic reaction in the liquid phase containing only one component (isobutylene), initiated by irradiation from an external light source. This would then be a method of producing known ions in the gas phase, but studying their reactions in condensed media. The composition of the medium is thus not limited but can be varied at will. Furthermore, the reactions of the ions can be studied in many cases without complicating free-radical side reactions, such as are often present in systems exposed to high energy radiation.

(7) (a) F. W. Lampe, *J. Phys. Chem.*, **63**, 1986 (1959); (b) V. L. Tal'roze and A. K. Lyubimova, *Dokl. Akad. Nauk SSSR*, **86**, 909 (1952).

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RECEIVED FEBRUARY 21, 1964

### Tetracyclo[3.3.0.0.<sup>4,6</sup>0<sup>2,8</sup>]octan-3-one. A Novel Dicyclopopyl Ketone

Sir:

In the course of studies directed toward a synthesis of bicyclo[3.2.1]oct-6-en-3-one, we have discovered a convenient route to the novel tetracyclo[3.3.0.0.<sup>4,6</sup>0<sup>2,8</sup>]octan-3-one (1). This ketone and the derived epimeric alcohols are conceivable precursors to a non-classical cation system such as 2. The present report relates the preparation, structure proof, and properties of 1.

