[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

# The Effect of Oxygen on the Reaction between Bromine and Butadiene

BY G. B. HEISIG AND H. M. DAVIS

That oxygen influences the rate of the addition of bromine to unsaturated hydrocarbons was shown by the work of H. S. Davis[1] on the determination of acetylenes by titration with bromine. Schultze[2] also showed the disturbing influence of oxygen in the titration of cyclopentadiene with bromine. More recently, Bauer and Daniels[3] reported that the rate of the reaction between solutions of bromine and cinnamic acid in carbon tetrachloride was rapid, even in the dark, in the absence of oxygen, but slow in its presence. These observations, together with the remarkable effects produced by the presence of oxygen and peroxides noted by Kharasch and his collaborators,[4] serve to emphasize the importance of the presence of oxygen on the rates of reactions. That this effect may not be general is suggested in the note of Deanesly,[5] which states that oxygen fails to produce any inhibitory effect on the addition of chlorine to olefinic hydrocarbons such as beta-butylene, although he admits that the reaction may be so fast that a retardation by oxygen may be difficult to detect. Since there were no quantitative data available to show whether oxygen affects the rate of addition of a halogen to an unsaturated hydrocarbon in the gas phase, it seemed desirable to investigate the problem. The reaction between gaseous bromine and butadiene in the presence of nitrogen containing about 0.3% of oxygen, studied by Heisig and Wilson,[6] was chosen for the investigation. The reaction between equal numbers of molecules of bromine and butadiene is bimolecular and occurs largely on the surface of the reaction vessel. The product is 1,4-dibromobutene. This study is of more than usual interest since it involves the effect of oxygen on the addition of bromine to a conjugated system.

The apparatus used in the previous investigation was altered to permit the preparation of gaseous reaction mixtures with increased oxygen content or with oxygen completely absent. In the first runs of the present study, the oxygen content of the reaction mixtures was increased from a partial pressure of 2 mm. of mercury to 375 mm. by using purified, dry, tank oxygen instead of nitrogen as the diluting gas employed to bring the initial pressure in the reaction sphere up to that of the atmosphere. The product under these conditions had a melting point of 46–47° instead of the 51–52° found for the product obtained from mixtures containing 0.3% of oxygen or from mixtures from which oxygen was excluded. Also, the rate of the reaction was somewhat slower than that observed when the partial pressure of the oxygen was 0.3%, as can be seen in Tables I and II.

TABLE I

TYPICAL RUNS. REACTION BETWEEN BROMINE AND BUTADIENE WITH VARIOUS CONCENTRATIONS OF OXYGEN

| Press. $O_2$ mm. | | 375 | 2 | Trace | Small trace | 0 |
|---|---|---|---|---|---|---|
| Run | | 8 | 10 | 11 | 12 | 13 |
| Min. | Sec. | Pressure drop of alpha-bromonaphthalene, mm. | | | | |
| 0 | 5 | 1.8 | 3.5 | 3.5 | 7.8 | 12.0 |
| | 10 | 3.5 | 6.2 | 6.2 | 11.4 | 15.0 |
| | 20 | 6.6 | 9.9 | 11.0 | 14.6 | 18.0 |
| | 30 | 9.3 | 12.4 | 14.5 | 16.7 | 19.8 |
| | 40 | 11.4 | 14.3 | 16.8 | 18.1 | 20.9 |
| | 50 | 12.9 | 15.8 | 18.5 | 18.8 | 21.6 |
| 1 | 0 | 14.2 | 17.1 | 19.8 | 19.4 | 22.1 |
| 1 | 30 | 16.8 | 20.1 | 22.5 | 20.6 | 22.8 |
| 2 | | 18.6 | 21.9 | 24.3 | 21.4 | 23.3 |
| 2 | 30 | 19.8 | 23.1 | 25.6 | 21.9 | 23.5 |
| 3 | | 20.8 | 24.0 | 26.5 | 22.2 | 23.7 |
| 4 | | 21.9 | 25.2 | 27.6 | 22.6 | 23.9 |
| 5 | | 22.9 | 25.9 | 28.2 | 22.8 | 24.5 |
| 7 | | 24.1 | 26.8 | 29.0 | 22.9 | 24.6 |
| 10 | | 25.0 | 27.3 | 29.7 | 23.3 | 24.7 |
| 15 | | 26.0 | 27.9 | 30.1 | 23.6 | 25.0 |
| 20 | | 26.2 | 28.3 | 30.3 | 23.9 | 25.3 |
| 30 | | 27 | 28.6 | 30.8 | 24.4 | 25.7 |
| ∞ | | 28.7 | 29.6 | 31.5 | 25.3 | 27.0 |

The apparatus was then modified so that the tank nitrogen was passed over hot, freshly reduced copper gauze. All parts of the apparatus were evacuated and then thoroughly flushed with the oxygen-free nitrogen. When nitrogen so treated was the only diluent used, the reaction rate was greater than that obtained when (untreated) tank nitrogen was the diluent. Moreover, the rate increased with subsequent runs, as would be expected with the progressive removal of the last traces of oxygen from the purifying

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(1) H. S. Davis, *et al.*, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

(2) Schultze, THIS JOURNAL, **56**, 1552–56 (1934).

(3) Bauer and Daniels, *ibid.*, **56**, 2014 (1934).

(4) Kharasch and Potts, *ibid.*, **58**, 57 (1936). This is the last published article.

(5) Deanesly, *ibid.*, **56**, 2501 (1934).

(6) Heisig and Wilson, *ibid.*, **57**, 859–63 (1935).

TABLE II

COMPARISON OF THE CURVES. TYPICAL DATA

| | | | | Slope when reaction is 80% completed | | | Slope when reaction is 67% completed | | |
|---|---|---|---|---|---|---|---|---|---|
| Run | $P_{O_2}$ mm.[a] | Total $-\Delta P$, exptl., mm.[b] | $\Delta t$ to initial reading, sec. | $-\Delta P$ of slope, mm.[b] | $\Delta t$ since start of reactn., sec. | Slope of tangt. | $-\Delta P$ of slope, mm.[b] | $\Delta t$ since start of reactn., sec. | Slope of tangt. |
| 8 | 375 | 28.7 | 25 | 17.2 | 120 | 17°55′ | 9.7 | 57 | 48° 5′ |
| 10 | 2 | 29.6 | 30 | 18.3 | 101 | 27° 8′ | 10.8 | 53 | 52°46′ |
| 11 | 0 (trace) | 31.5 | 25 | 20.2 | 88 | 27°38′ | 12.7 | 49 | 59°59′ |
| 12 | 0 (small trace) | 25.3 | 20 | 14.0 | 38 | 53°17′ | 6.5 | 24 | 80°30′ |
| 13 | 0 | 27.0 | 20 | 15.7 | 32 | 60°28′ | 8.2 | 22 | 84°12′ |

[a] Pressure given in mm. of mercury. [b] Pressure given in mm. of alpha-bromonaphthalene.

train. The product had the same appearance and melting point as that obtained when tank nitrogen (0.3% oxygen) was used.

The reaction was fast in all cases; in fact, somewhat more than half of the reaction took place in the twenty to thirty seconds required to mix the gases before the first reading could be made. The vapor pressure of the product is about 13 mm. of alpha-bromonaphthalene. When the first reading is made the gases in the reaction sphere are already saturated with product and a sufficient amount has been formed to cover the surface with a monomolecular layer.

It will be noted in Table II that the total observed pressure drop is somewhat smaller in the runs in which no oxygen was present, although the time required to make the first reading is less. This is in agreement with the other evidence that the reaction is faster in the absence of oxygen, since it indicates that a greater part of the reaction occurs before the first reading can be taken.

For ready comparison of the rates of the reactions, a curve for each experiment was prepared by plotting observed pressure drop against time. The slopes of the tangents to the curves when 80% of the calculated pressure drop has occurred, increase as the proportion of oxygen in the mixture decreases, as can be seen from column 7 in Table II. The greater the angle, the more rapidly is the reaction taking place. This is not a fortuitous coincidence, for the slopes determined when 66.7% of the reaction is completed increase in the same order. Furthermore, the time required for 80 and 66.7% of the reaction to take place decreases with the amount of oxygen present, as can be seen in columns 6 and 9 of Table II.

Since the rate of the reaction is sensitive to a small concentration of oxygen, and since the earlier work showed that the reaction occurred largely on the surface, a reasonable mechanism is that chains are initiated at the wall of the reaction vessel, and are broken by the oxygen. The data however do not exclude a mechanism in which the reaction occurs wholly on the surface and the rate of the reaction is decreased because of the occupation of the "active spots" on the surface by oxygen.

**Experimental.**—The apparatus was that described by Heisig and Wilson.[6] It was modified by the introduction of an electrically heated roll of copper screen to remove the 0.3% of oxygen in the tank nitrogen before it passed into the purifying and drying train. Before each run, the hot copper gauze was subjected to a long treatment with a stream of hydrogen under a pressure of one atmosphere, thus ensuring an active surface. A connection was also provided to permit purified oxygen to be mixed with the butadiene used in the experiment. This was a metal-to-glass connection. The oxygen was scrubbed by passage through three double wash bottles filled with a 40% solution of potassium hydroxide, and was dried by passage through calcium chloride and then through resublimed phosphorus pentoxide. The butadiene and bromine were portions of preparations of these substances used in the previous investigation. The reaction vessel had a volume of 53.8 cc. The slopes of the tangents to the curves were determined by a variation of the method described by Lipka.[7]

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## Summary

The reaction between equimolar mixtures of bromine and butadiene has been studied in the presence of a partial pressure of oxygen at 375 mm., 2 mm. (Hg), and in the absence of oxygen, the total pressure of the reaction mixture being equal to that of the atmosphere.

The rate of the reaction as measured by the

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(7) Joseph Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, Inc., New York (*ca.* 1919): Part II, Article 110, page 255.

slopes of the tangents to the curves (of pressure-drop against time) when 80 and 67% of the gases have reacted, increases with the decrease of oxygen in the mixture. The increase in the rate is especially noticeable when the partial pressure of oxygen is well below 2 mm.

The sensitivity of the rate of the reaction to small amounts of oxygen, together with the evidence that the reaction occurs largely at the surface, suggests a chain mechanism with short chains initiated at the surface.

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# Organic Nitrogen Bases from Pyrolysis of Cottonseed Meal[1]

BY IVY PARKER, C. L. GUTZEIT, A. C. BRATTON AND J. R. BAILEY

## Introduction

Research on the bases in petroleum distillates[2] has shown a preponderance of non-aromatic types, not previously obtained from any other natural source. On the assumption that petroleum is of vegetable or animal origin, it may be assumed that carbohydrates and fats, as well as proteins, contributed to the formation of nitrogen compounds; in any event an explanation of the genesis of non-aromatic petroleum bases, among which are probably compounds of cyclopentane structure, might have an important bearing on the origin of petroleum itself.

In an attempt to determine whether similar non-aromatic bases would result from pyrolysis of a material containing proteins, carbohydrates and fats, the present investigation was undertaken. The Union Oil Company of California contributed 337 pounds of crude bases obtained from the distillation of 23 tons of cottonseed meal with nitrogen-free lubricating oil as a liquid medium, through which low temperature pyrolysis could be controlled.[2a]

Previous work by other investigators on bases formed in protein pyrolysis are of little interest as concerns the present investigation, because in these studies pure proteins were employed.[3]

The complexity of the cottonseed meal bases is comparable with that of petroleum bases. An unexpected difference is that, unlike bases from other important natural products, those from protein material are at least 50% *petroleum ether insoluble* and, besides, the higher boiling fractions have a much greater nitrogen content than can be accounted for on the assumption of a single nitrogen in the molecule. Furthermore, there is no evidence of naphthenic structure, such as is highly probable for certain petroleum bases. From the lower boiling fractions there have been isolated pyridine, and a number of its homologs, identical with products from coal, shale or bones.

The coal tar bases, quinoline, isoquinoline, quinaldine and lepidine, along with the kero base, 2,3,8-trimethylquinoline[2b] (p. 1245), have been found. A beautifully crystallizing diazine, $C_{11}H_{14}N_2$, of undetermined structure is probably a dihydroquinazoline, as indicated by its amphoteric character.

Upon vacuum distillation of the high boiling protein bases in an atmosphere of nitrogen, colorless distillates are obtained which, unlike corresponding petroleum base cuts, soon darken and precipitate tar. This instability renders difficult the isolation of individual products. So far the petroleum ether insoluble bases have been only superficially studied.

In the boiling range of 135 to 172° a total of 876 cc. (14 fractions) of petroleum ether soluble material was available with $d^{25}_4$ values between 0.9418 and 0.9652 and $n^{25}_D$ values between 1.4947 and 1.4992. These physical constants clearly indicate a preponderance of pyridines. From the high nitrogen content of these fractions pyrazines and pyrimidines were suspected but a search for diazines was fruitless. The comparatively small volume of material in this range can be attributed

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(1) In part from dissertations submitted by Ivy May Parker and C. L. Gutzeit to the Faculty of the Graduate School of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1935.

(2) (a) E. J. Poth, W. D. Armstrong, C. C. Cogburn and J. R. Bailey, *Ind. Eng. Chem.*, **20**, 83 (1928); (b) E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. W. Floyd and J. R. Bailey, THIS JOURNAL, **52**, 1239 (1930); (c) W. C. Thompson and J. R. Bailey, *ibid.*, **53**, 1002 (1931); (d) B. F. Armendt and J. R. Bailey, *ibid.*, **55**, 4145 (1933); (e) G. R. Lake and J. R. Bailey, *ibid.*, **55**, 4143 (1933); (f) T. S. Perrin and J. R. Bailey, *ibid.*, **55**, 4136 (1933); (g) B. S. Biggs and J. R. Bailey, *ibid.*, **55**, 4141 (1933); (h) R. W. Lackey and J. R. Bailey, *ibid.*, **56**, 2741 (1934).

(2a) The preliminary work in this connection was carried out in the Texas Laboratory by Ivy Parker.

(3) Pictet and Cramer, *Helv. Chim. Acta*, **2**, 188 (1919); T. B. Johnson and Daschavsky, *J. Biol. Chem.*, **62**, 197 (1924).