

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Peroxide Effect in the Addition of Reagents to Unsaturated Compounds. XI. The Solvent Effect in the Addition of Hydrogen Bromide to Isobutylene

BY M. S. KHARASCH AND W. M. POTTS

Introduction

There are many discrepant conclusions recorded in the literature regarding the effect of solvents on the direction of addition of hydrogen bromide to ethylene compounds containing a double bond at the end of the chain. Although our exhaustive study of allyl bromide¹ and other substances indicated to us that the effect of solvents was on the velocity rather than on the direction of addition,² nevertheless, we felt that another thorough study of the effect of solvents was in order. Isobutylene was selected as the test unsaturated compound because it is little sensitive to the "peroxide" effect. In consequence thereof, we hoped to obtain without great difficulties, if our hypothesis were correct, the "normal" reaction product in quantitative yields, irrespective of the solvent. The addition of small quantities of peroxides to such a system should, therefore, enable us to bring out most strikingly the "peroxide" effect. A further consideration in this selection of isobutylene was that such factors as time of addition, light, and temperature were shown by us to have no effect upon the direction of addition of hydrogen bromide to it.

In an able paper, Ingold and Smith³ enumerate the following factors that might affect orientation at the double bond: "electrical effects, dielectric constants, electrical saturation effects including influences due to electrostriction and molecular and field anisotropy, and the interactions of quadrupoles and higher multipoles with one another and with dipoles, and to distortion effects. The statistical calculation of these combined effects is not possible at present.

"These component forces all contribute to the internal pressures of liquids but so also does the effect of quantum-mechanical reciprocal perturbations."

These statements, of course, carry with them as yet no predictive possibilities. The authors

(1) Kharasch and Mayo, *THIS JOURNAL*, **55**, 2468 (1933).

(2) A pertinent quotation from one of our earlier articles¹ is perhaps in order. With reference to the effect of solvents, we state that they affect "only those reactions which are peroxide-catalyzed, but have no effect on reactions which are little sensitive to peroxides."

(3) Ingold and Smith, *J. Chem. Soc.*, 2746 (1931).

quoted, however, in reviewing the field, feel that the direction of addition of halogen acid to unsaturated compounds in solvents should be governed not by the dielectric constant of the solvent but rather the internal pressure. In support of this they cite some experiments on the addition of hydrogen iodide to propylene in which the percentage of normal propyl iodide formed decreased as the internal pressure of the solvents increased in value. It should be stated that no such effects were observed by us in the study of addition of hydrogen bromide to propylene.

Sherrill, Mayer and Walter⁴ conclude that the directive addition of hydrogen bromide to pentene-1 and heptene-1 is controlled by the solvent but not by the peroxide content of the material. Similarly, Linstead and Rydon⁵ believe that the peroxide effect is of "secondary importance" in the addition of hydrogen bromide to allyl acetic acid in solvents such as hexane.

Extensive general experience in this Laboratory, supplemented by the specific study of Kharasch, Hinckley and Gladstone⁶ on the addition of hydrogen bromide to pentene-1, has convinced the present authors that peroxide-free reaction conditions are almost impossible to attain (in the cases of additions which are particularly sensitive to peroxide catalysis) except under vacuum technique, accompanied by the most rigorous purification of *solvents and addition reagents* as well as of the unsaturated compound under investigation. However, all previous work in this Laboratory indicates that the results obtained by the most rigid oxygen-exclusion technique may be duplicated in ordinary laboratory procedure by the simple expedient of adding small quantities of antioxidants to the reaction system. So far as we have ever been able to determine, the added antioxidant has absolutely no effect on the course of the reaction save the purely negative one of eliminating peroxide catalysis.

If this view of antioxidant function be valid, then the study of Kharasch, Hinckley and Glad-

(4) Sherrill, Mayer and Walter, *THIS JOURNAL*, **56**, 928 (1934).

(5) Linstead and Rydon, *Nature*, **132**, 643 (1933); *Cf.* also Bee-man, Linstead and Rydon, *J. Chem. Soc.*, 568-76 (1933).

(6) Kharasch, Hinckley and Gladstone, *THIS JOURNAL*, **56**, 1642 (1934).

stone already cited⁶ must be interpreted as demonstrating conclusively that the direction of addition of hydrogen bromide to pentene-1 is independent of the solvent. Unpublished work by Kharasch and McNab^{6a} would lead to a similar conclusion concerning the addition of hydrogen bromide to allylacetic acid.

We interpret the supposed directive solvent effect observed by other workers under other experimental conditions as an influence of the solvent (and conceivably in some cases of solvent impurities) upon the relative rates of the "normal" and peroxide-catalyzed addition reactions.

Addition of Hydrogen Bromide to Isobutylene in Solvents.—In the previous work⁷ on the addition of hydrogen bromide to isobutylene, glacial acetic acid and xylene were the only solvents employed. To make a further investigation of the solvent effect, it was decided to carry out the addition of hydrogen bromide to isobutylene employing a number of solvents that showed a wide variation in the values of their dielectric constants and internal pressures. For convenience in carrying out these additions and in analyzing the products of the reactions, the following solvents were used: pentane (1.83), carbon disulfide (2.6), propionic acid (3.2), ethyl bromide (9.4), benzonitrile (26.4), nitrobenzene (36.1) and water (80). The dielectric constant of each solvent is indicated in parentheses.

The technique employed in these additions was the same as that described in previous papers from this Laboratory.^{2,6,7} It should be pointed out, however, that the tubes containing the reaction mixtures were removed from the bath as soon as the seal had cooled, and that the contents soon reached room temperature. Even though some of the components may have solidified, this condition was only of short duration.

Two types of runs were made with each solvent: runs in which a peroxide (ascari-dole) was added and the air was left in the tubes, and runs in which an antioxidant (diphenylamine) was used, and in these runs the tubes were evacuated to a pressure of 1×10^{-4} mm. while the reagents were frozen in liquid nitrogen baths.

The analyses of the products of the additions was effected by employing both the boiling points and the refractive indices. The index for tertiary butyl bromide is 1.4275–1.4277, and for the

(6a) This article has now been published in *J. Chem. Ind.*, **54**, 989 (1935).

(7) Kharasch and Hinckley, *This Journal*, **56**, 1243 (1934).

isobutyl bromide, 1.4355. In all the experiments the composition of the mixture was made certain by repeated washing of it with sodium carbonate solution, and the determination of the index of refraction and boiling point of the dried material.

It is quite evident from a consideration of Table I that the non-catalyzed peroxide-free addition is absolutely independent of the solvent. In all cases tested, *t*-butyl bromide was the exclusive product of the reaction under antioxidant conditions. Upon the basis of these data, there is no reason to assume that either the dielectric constant or the internal pressure of the solvent have anything to do with the direction of addition. Furthermore, we believe that the solvents selected covered a sufficiently wide range (in the dielectric constants from 1.83 to 80) to justify the extension of this conclusion to all solvents.

In the presence of peroxides, the order of addition of hydrogen bromide to isobutylene is reversed, and isobutyl bromide is the product of the reaction. It might appear at a first glance that in these cases a definite solvent effect is evident. However, our own feeling is that such an assumption is without any foundation. One must bear in mind that the addition of hydrogen bromide to isobutylene is very fast—so that the velocity of addition in the presence of peroxides must proceed at a tremendously accelerated rate compared with the "normal" addition. With two fast reactions one must therefore maintain truly "peroxide" conditions at all times, in order to obtain the "abnormal" product exclusively. The amount of peroxide needed to accomplish that result varies somewhat with the solvent and the speed of addition of the hydrogen bromide. This was confirmed experimentally in the case of nitrobenzene as the solvent. In the presence of 0.04 mole of ascaridole, the yield of isobutyl bromide was only 75% and that of *t*-butyl bromide, 25%. However, when 0.06 mole of ascaridole was used, and the hydrogen bromide was led into the reaction mixture very slowly, we were able to obtain 97% of the isobutyl bromide.

We are fairly certain, therefore, that with slight modifications hydrogen bromide can be made to add to isobutylene in all solvents to yield isobutyl bromide exclusively, if rigorous peroxide conditions are maintained.

These additional data thus confirm and extend our earlier statement that under rigidly maintained peroxide and antioxidant conditions, sol-

TABLE I
 ADDITION OF HYDROGEN BROMIDE TO ISOBUTYLENE IN SOLVENTS

Solvent	Pentane (1 M)	CS ₂ (1.2 M)	Propionic acid (0.9 M)	Ethyl bromide (1 M)	Benzo- nitrite (0.7 M)	Nitro- benzene (0.9 M)	Water (0.9 M)
A. Addition in the Presence of Peroxides							
Ascaridole, M	0.03	0.04	0.04	0.03	0.04	0.04	0.04
Isobutylene $\left\{ \begin{array}{l} \text{g.} \\ \text{M} \end{array} \right.$	17	13	15	12	11	13	13
HBr $\left\{ \begin{array}{l} \text{g.} \\ \text{M} \end{array} \right.$	0.3	0.23	0.27	0.21	0.20	0.23	0.23
B. p. of reaction mixture, °C.	27.5	24	25	19	21	21	25
Yield $\left\{ \begin{array}{l} \text{g.} \\ \text{\%} \end{array} \right.$	1.1	1.3	1.1	1.1	1.3	1.2	1.3
n^{20}_D	71.5-91.5	87.5-91	70-90	70-90	73-91.5	72-91	70-91.5
<i>t</i> -Butyl bromide, %	33	26.5	31.5	26	20	29	28.5
Isobutyl bromide, %	79	86	86	88	74	94	92
Reaction mixture washed with sodium bicarbonate and water, dried with anhydrous sodium sulfate, and distilled	1.4338	1.4357	1.4345	1.4338	1.4338	1.4335	1.4345
B. p., °C.	22	0	13	22	22	25	13
n^{20}_D	78	100	87	78	78	75	87
B. Addition <i>in Vacuo</i> and in the Presence of Antioxidants							
Solvent	Pentane (0.8 M)	CS ₂ (1.3 M)	Propionic acid (1 M)	Ethyl bromide (1 M)	Benzo- nitrite (0.5 M)	Nitro- benzene (0.9 M)	Water (1.5 M)
Diphenylamine, M	0.03	0.03	0.03	0.03	0.03	0.04	0.03
Isobutylene $\left\{ \begin{array}{l} \text{g.} \\ \text{M} \end{array} \right.$	13.5	12.5	12.5	13.5	10.5	12	20.5
HBr $\left\{ \begin{array}{l} \text{g.} \\ \text{M} \end{array} \right.$	0.24	0.22	0.22	0.24	0.19	0.21	0.37
B. p. of reaction mixture, °C.	23.5	22	20	24	18	23	35
Yield $\left\{ \begin{array}{l} \text{g.} \\ \text{\%} \end{array} \right.$	1.2	1.2	1.1	1.2	1.1	1.3	1.2
n^{20}_D	69-73	52-72	69-73	63-73	71.5-72.8	73-73.3	71.5-72.8
Reaction mixture washed with sodium bicarbonate and water, dried with anhydrous sodium sulfate, and distilled	27.5	25.5	28	27.5	22	23.5	42.5
B. p., °C.	83	83	92	83	86	80	85
n^{20}_D	1.4267	1.4294	1.4278	1.4271	1.4272	1.4278	1.4271
B. p., °C.	72.5-72.7	71.5-72.1	72-72.7	72-73	71.5-72	71.6-72.6	72.2-72.5
n^{20}_D	1.4267	1.4278	1.4275	1.4270	1.4271	1.4273	1.4271

vents *per se* have an effect on the velocity but not on the direction of addition.

Summary

1. Pure tertiary butyl bromide is formed by the addition of hydrogen bromide *in vacuo* to isobutylene in the presence of solvents and antioxidants.

2. Isobutyl bromide is formed in amounts varying from 100 to 75% by the addition of hydrogen bromide to isobutylene in the presence of solvents, air and peroxides.

3. The conclusion is reached that under rigidly maintained antioxidant conditions solvents *per se* have no effect upon the direction of addition of hydrogen bromide to isobutylene, but affect markedly the rate of addition. We interpret this conclusion as indicating that the apparent directive solvent effect observed under other than antioxidant conditions is in reality an effect of the solvent upon the relative rates of the "normal" and peroxide-catalyzed addition reactions.

CHICAGO, ILLINOIS

RECEIVED OCTOBER 26, 1935