tion on the mechanism of presumably simple organic reactions under presumably simple conditions.

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Summary

The addition of hydrogen chloride to isobutylene in heptane solution at 0° was studied by a dilatometric method. *t*-Butyl chloride was the only product found. The addition was greatly accelerated by traces of water, mercury and phosphorus pentoxide, all of which were difficult to exclude completely, and the experiments were therefore not entirely reproducible. The uncatalyzed reaction seems to be of third order with respect to hydrogen chloride and of first order with respect to isobutylene, while the catalyzed reaction approximates second order. An addition proceeding at 0° is greatly accelerated by cooling to −80° or below and then warming to 0°. The high order of the addition and the unusual effect of temperature can be accounted for if hydrogen chloride–isobutylene complexes are involved in the reaction, but the possibility that the addition is a chain mechanism of the ionic type has not been excluded.

PASSAIC, N. J. RECEIVED AUGUST 21, 1946

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

The Addition of Hydrogen Bromide to Propylene[1]

BY FRANK R. MAYO[2a] AND MICHAEL G. SAVOY[2b]

The first attempt in this Laboratory to study the kinetics of the normal addition of halogen acids to alkenes was made with hydrogen bromide and propylene in *n*-pentane solution. A rapid abnormal addition to give *n*-propyl bromide always occurred unless an inhibitor for the abnormal addition was also present. The inhibitor was not always effective, however, and its use introduced other complications. The present effort was finally abandoned in favor of work on the hydrogen chloride–isobutylene system.[3] Nevertheless, the results obtained are of interest in showing the difficulties encountered in working with this system and in supporting and extending the conclusions of the other paper.

Experimental

In general, the apparatus and procedures were much like those used for hydrogen chloride and isobutylene[3]; only differences are indicated below.

Propylene was obtained from the Carbide and Carbon Chemicals Corp. Hydrogen bromide was prepared from tetralin and bromine and then passed through naphthalene to remove unreacted bromine. Both reactants were distilled from phosphorus pentoxide and stored as liquids at −78° in 200-cc. bulbs permanently attached to the vacuum line. For inhibitors of abnormal addition, 2,4-di-*t*-amylphenol (Sharples Solvents Co.), thiophenol and thiocresol (Eastman Kodak Co.) were employed, samples being distilled *in vacuo* just before use. A good grade of *n*-pentane was kindly supplied by the Universal Oil Products Co.

The dilatometers for the 0° experiments had a volume of about 40 cc. The stems were made from 6 mm. o.d. tubing, had a volume of about 0.12 cc. per cm. of length, and ended above the stem in 2–5 cc. safety bulbs. The liquid levels were read from 30 cm. scales, graduated in 2 mm. intervals. Before use, the dilatometers were strongly heated at reduced pressure, cooled, and filled with carbon dioxide. The inhibitor, dissolved in 3 cc. of *n*-pentane, was then added to the dilatometer. This solution was frozen and the system was evacuated. The remaining *n*-pentane, propylene and hydrogen bromide were then distilled into the dilatometer in that order and without special precautions to exclude mercury vapor, but otherwise according to the procedure previously described. After the dilatometers were sealed off, the contents were melted and mixed by shaking at −78° and then were allowed to warm, over a period of about five minutes, to about 10° below the thermostat temperature. This point, at which the dilatometer was put in the thermostat, was arbitrarily taken as zero time. Scale readings were then taken frequently over a period of ten to twenty minutes, during which the meniscus level rose to a maximum in a minute or two and then began to decrease regularly. This regular decrease, extrapolated back to zero time, gave the initial scale reading and the volume used for calculating concentrations. At the end of the reaction, the dilatometer contents were shaken into water, washed, separated, dried and distilled through a Podbielniak column. The addition product was then identified by boiling point and refractive index[4] and the washings were titrated for hydrogen bromide. No rate constants were calculated for any experiment in which the addition product contained *n*-propyl bromide.

The volume change per mole of isopropyl bromide formed was calculated for every experiment where this halide was the sole product, assuming that no reaction occurred before "zero time." In experiments at 30°, the following values were obtained: 29.00, 28.57, 28.48, 28.28, 28.03, 27.10, 26.87, 21.50 cc./mole. (The last experiment contained 100% excess hydrogen bromide.) From these results the volume change at 30° was arbitrarily taken to be 29.0 cc./mole. In experiments 4, 7, 8 and 9 at 0° (with higher initial concentrations of reactants) values of 22.51, 22.64, 25.58 and 27.93 cc./mole were observed. On the basis of these values and the 30° result, the volume change at 0° was taken as 28.0 cc./mole and calculations on experiments 4, 7 and 8 were made on that basis.

Results

It has been reported previously from this Laboratory[4] that the addition of hydrogen bromide to

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[1] This paper is based on the Master's Thesis of M. G. Savoy, June, 1941. Some of the results were presented before the Division of Organic Chemistry at the St. Louis Meeting of the American Chemical Society, April 9, 1941.

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[3] Mayo and Katz, THIS JOURNAL, **69**, 1339 (1947).

[4] Kharasch, McNab and Mayo, *ibid.*, **55**, 2531 (1933); **56**, 1425 (1934).

propylene in the absence of a solvent yields isopropyl bromide in the presence or absence of air but *n*-propyl bromide in the presence of peroxides. However, in the early stages of the present work, it was found that solutions of propylene and hydrogen bromide in pentane gave rapid and nearly complete formation of *n*-propyl bromide, the abnormal addition product, even though air and peroxides were carefully excluded. For example, although one solution 1.2 molar in each reactant was kept overnight at −78° without appreciable volume change, when brought to 0° the volume remained constant for about five minutes and then dropped rapidly to a value which did not change further in two days. The reaction was found to be 98.5% complete and the product was *n*-propyl bromide. The pentane used in this experiment had previously been found to be free from peroxides and air was removed carefully from the dilatometer. Similar abnormal additions were frequently obtained even in the presence of common inhibitors of the abnormal addition.[5] In the presence of inhibitors, films or second layers occasionally formed in the dilatometers, sometimes after the reaction had proceeded for some time. Phase separation seemed to be accompanied by a faster, lower-order reaction. These difficulties led to initiation of work with hydrogen chloride and isobutylene.[3]

Starting with an equimolecular mixture of propylene and hydrogen bromide without solvent at 0°, Maass and Wright[6] found that 22% of the propylene and 11% of the hydrogen bromide were converted to a hexyl bromide. This conclusion was qualitatively confirmed in this Laboratory[7] but we never found any appreciable quantity of hexyl bromide in our additions in pentane solution, nor of any other reaction products other than the propyl bromides.

Results of normal additions at 0°, summarized in Table I and Fig. 1, will be considered first. With equal concentrations of reagents, about three days were required for 60% reaction, the rate dropping off rapidly with time. As in the previous paper,[3] rate constants are calculated for intervals, not from the beginning of the reaction. Figure 1 shows the rate constants for successive intervals in each run plotted (on a logarithmic scale) against the concentration of hydrogen bromide (or propylene, if lower) at the ends of those intervals. Three experiments cover the concentration range from about 2 molar to 0.8 molar while the last covers a slightly greater range. Of four other unrecorded experiments in the same range, two without antioxidant gave only abnormal addition and two with antioxidants (diamylphenol or *p*-nitrosotoluene) gave mixtures of propyl bromides.

TABLE I

THE NORMAL ADDITION OF HYDROGEN BROMIDE AND PROPYLENE AT 0°[b]

Expt.	Time,[a] min.	[HBr] or $[C_3H_6]$* moles/liter	$k_2 \times 10^3$ for [H][U]	$k_3 \times 10^3$ for $[H]^2[U]$	$k_3 \times 10^3$ for $[H][U]^2$	$k_4 \times 10^3$ for $[H]^2[U]^2$	$k_4 \times 10^3$ for $[H]^3[U]$
(4)	Contained 18.6 g. pentane and 0.2 g. thiocresol; initial volume, 39.96 cc. Yellowish film on dilatometer wall.						
	0	1.963	$[HBr]_i = [C_3H_6]_i = 2.269$ moles/liter				
	72	1.753	0.847	0.456		0.248	
	118	1.616	1.065	.620		.371	
	250	1.417	0.658	.438		.289	
	505	1.197	.506	.390		.333	
	1485	0.783	.449	.476		.509	
	2000	.699	.299	.402		.545	
(7)	Contained 20.4 g. pentane and 0.2 g. di-*t*-amylphenol; initial volume 41.02 cc.						
	0	1.922	$[HBr]_i = [C_3H_6]_i = 2.192$ moles/liter				
	55	1.718	1.13	0.617		0.339	
	175	1.512	.658	.408		.255	
	385	1.360	.352	.245		.171	
	715	1.220	.257	.200		.158	
	1465	1.044	.181	.163		.157	
	3025	0.862	.118	.137		.140	
	4885	.750	.093	.116		.145	
(8)	Contained 14.2 g. pentane and 0.3 g. di-*t*-amylphenol; initial volume 37.15 cc.						
	0	2.272	$[HBr]_i = 2.400$ moles/liter. $[C_3H_6]_i = 4.150$ moles/liter.				
	56	2.130	0.294	0.133	0.074	0.0338	0.0607
	197	1.958	.159	.076	.042	.0193	.0381
	595	1.634	.129	.072	.037	.0200	.0406
	865	1.476	.114	.073	.035	.0222	.0478
	1635	1.229	.077	.057	.025	.0183	.0426
	2305	1.090	.062	.054	.021	.0183	.0463
	3475	0.899	.061	.061	.022	.0218	.0620
(9)	Contained 14.2 g. pentane and 0.3 g. di-*t*-amylphenol; initial volume 38.30 cc.						
	0	2.929*	$[HBr]_i = 4.706$ moles/liter. $[C_3H_6]_i = 2.929$ moles/liter				
	39	2.464*	0.993	0.224	0.370	0.082	0.0506
	99	1.899*	1.101	.280	.513	.132	.0710
	256	1.156*	0.970	.299	.667	.207	.0914
	837	0.488*	.584	.232	.818	.330	.0922
	1196	.367*	.360	.163	.857	.391	.0744
	1701	.273*	.280	.133	.889	.425	.0636

[a] Time was measured from the point at which the dilatometer contents reached about −10°. In expts. 4, 7 and 8 appreciable reactions occurred before this point and the concentrations at zero time were calculated from the initial concentrations $[HBr]_i$, and $[C_3H_6]_i$ and the volume change per mole reacting. [b] Rate constants calculated from equations 2, 3, 5, 6, 8, 10, 11 in ref. (3).

All the second order rate constants decrease as the reaction progresses, showing that the reaction is at least partly of higher order. In the calculation of third and fourth order constants, better agreement is obtained between the experiments with excess propylene (no. 8) and hydrogen bromide (no. 9) when the reaction is assumed to have a higher order with respect to hydrogen bromide

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(5) Unsuccessful attempts were made to obtain an abnormal addition of hydrogen chloride by taking advantage of this effect. In one experiment, 0.136 mole of hydrogen chloride, 0.09 mole of propylene and 190 cc. of *n*-heptane were allowed to stand for fourteen days at room temperature in a sealed Pyrex tube. The mixture was then exposed to a mercury lamp for five hours. In another experiment, 0.136 mole of hydrogen chloride, 0.119 mole of propylene, 1.0 g. of benzoyl peroxide and 75 cc. of heptane were heated to 100° for four hours. No addition occurred in either experiment.

(6) Maass and Wright, THIS JOURNAL, **46**, 2664 (1924).

(7) In the presence of benzoyl peroxide under these conditions, little or no hexyl bromide is formed along with the *n*-propyl bromide. Hexyl bromide formation is therefore associated with the normal addition reaction.

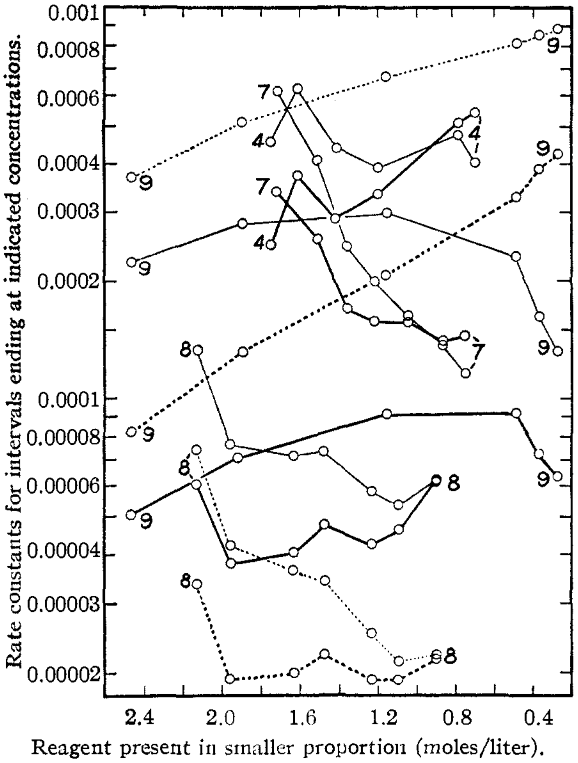

Fig. 1.—Rate constants for the normal addition of hydrogen bromide to propylene. Light lines join third order rate constants based on $[HBr]^2[C_3H_6]$ (solid lines) or $[HBr][C_3H_6]^2$ (broken lines). Heavy lines join fourth order rate constants based on $[HBr]^3[C_3H_6]$ (solid lines) or $[HBr]^2[C_3H_6]^2$ (broken lines).

than to propylene. These two experiments not only agree with each other better on a fourth order than on a third order basis, but they also agree better with Expt. 7 (where reactant concentrations are equal) in the concentration range near 1 molar where the constants show the least drift. Further, the fourth order constant drifts less in expt. 7 than the third order constant although there is not much choice in expts. 8 and 9. The dilatometer in expt. 4 developed a yellow film on the walls. This run reacted faster than Expt. 7, and in contrast with the latter experiment, the fourth order constants for successive intervals tended to rise. The second phase thus exerted an effect somewhat like that of water in the hydrogen chloride–isobutylene experiments, but in the present experiments, when no second phase separated, the high reagent concentrations apparently obscured any effect of the inhibitors on the homogeneous reaction.

Preliminary experiments on the reaction of hydrogen bromide with propylene in alcohol and ether solution support the conclusion that hydroxylic compounds catalyze the reaction. A 2:2:1 molar mixture of absolute alcohol, hydrogen bromide and propylene reacted completely as soon as the cold reaction mixture melted, yielding chiefly isopropyl bromide and ethyl bromide. A 1:1.7:1 molar mixture of fresh anhydrous ether, hydrogen bromide and propylene reacted almost as fast but gave some *n*-propyl bromide in addition to isopropyl bromide, ethyl bromide and, presumably, alcohol.

The agreement between the fourth order rate constants in experiments 7, 8 and 9 can be improved if allowance is made for complex formation between the propylene and hydrogen bromide, using equations 13, 16 and 17 in the previous paper.[3] Taking k_4 in the respective experiments as 0.00016, 0.000043 and 0.000090 when the concentration of hydrogen bromide (or propylene, if lower) is 1.2 molar, concentrations of complex were calculated for K (equilibrium constant for complex formation) = 0.1, 0.3, 0.5 and 1.0, and then the corrected rate constant, k_4', based on concentrations of free instead of total reactants, was calculated. The best results were obtained with K = 0.3, the respective values of k_4' being 0.000434, 0.000271 and 0.000275. The ratio of the largest to the smallest constant is thus reduced by the correction for complex from 3.72 to 1.62. At this concentration range, expt. 8 shows the largest increase in k_4' for a given increase in K, the excess propylene reducing the effective concentration of hydrogen bromide which appears to the third power in the rate equation. Trial has shown that such a correction in the range 2.0–1.2 molar increases somewhat the drift of k_4' with time in expt. 7, improves the result slightly in 9, and has no effect in 8.

The experiments at 30° will be considered next although they are not worth recording in detail. In order to work in more dilute solutions and still obtain sufficient reaction product for easy identification, a dilatometer of 100 cc. volume was employed and initial concentrations were reduced to 0.9 molar or less. The higher temperature was used to obtain higher reaction rates. In attempts to obtain fewer abnormal additions and more reproducible rates, about twenty experiments were carried out at 30°, all but one with equal concentrations of reactants. Of these experiments, only eight gave a normal addition reaction. The remainder gave only *n*-propyl bromide. All the eight successful experiments were obtained in groups after recent thorough cleanings of the vacuum line.[8] Thus repression of abnormal addition became more difficult in the more dilute solutions at 30°. Of the eight normal runs obtained three showed definite evidence of a second phase, reacted two to three times as fast as the others, and gave rate constants corresponding better to a second than to a higher order reaction. The other five experiments were unfortunately stopped at less than 50% reaction and gave no clear indication of order. Although the qualitative agree-

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[8] These eight experiments employed 0.3–0.7 g. of diamylphenol for about 0.09 mole of each reactant. Of ten abnormal experiments on which records are currently available, five used diamylphenol, one used thiophenol, and three used thiocresol.

ment between the last five experiments was good, the rate constants in any single experiment varied erratically, suggesting that temperature control on the thermostat, and therefore dilatometer readings, were unsatisfactory. The initial fourth order rate constants for these experiments fall in the range 0.0002 to 0.0005 at concentrations of about 0.85 molar. The comparable final stages of expt. 7 at 0° gave $k_4 = 0.00015$, suggesting that a temperature change from 0 to 30° may double or triple the rate of reaction.

Conclusions

The most unexpected information obtained from this research was the effect of dilution in promoting the abnormal chain mechanism addition of hydrogen bromide. Previous work with allyl bromide[9] and isobutylene[10] had shown that moderate dilution of a reaction mixture with an inert solvent facilitated abnormal addition, but the present work demonstrated that sufficient dilution made abnormal addition difficult to *repress*, even with careful exclusion of air and peroxides and use of inhibitors. The quantities of catalytic impurities remaining must have been minute, and either the chain lengths in the abnormal addition are extraordinarily great (or the chains are branched) or else some chains start without assistance from catalysts, or both. It is clear how dilution retards the normal addition, but it is difficult to see how dilution alone could *accelerate* the chain addition unless concentrated (but not dilute) hydrogen bromide–propylene mixtures contain a weak inhibitor for the abnormal addition, *e. g.*, the hydrogen bromide–propylene complex, or unless the rate of chain termination is unexpectedly low in dilute pentane solution. The dilution effect found in the early stages of this work has since been used to obtain abnormal additions, which are otherwise difficult to observe, of hydrogen bromide to 2-bromo-2-butene, trimethylethylene and styrene.[11]

In view of the present results, the confusion and controversies surrounding the effects of solvents on hydrogen bromide additions[12] now do not seem surprising. The present work also shows that, in the absence of information concerning the mechanism of addition, some work on the rates of addition of hydrogen bromide[13] and on the effects of alkyl halides on such additions[14] are open to some question.

The kinetic work reported here shows that the normal addition of hydrogen bromide to propylene in the presence of inhibitor is much like the addition of hydrogen chloride to isobutylene. Although the results are not clear-cut, the addition seems to be of third order with respect to hydrogen bromide and of first order with respect to propylene. On the basis of fourth order rate constants at 0°, the normal hydrogen bromide–propylene reaction is only 5–10% as fast as the hydrogen chloride–isobutylene reaction. Hence a much higher concentration range was studied where accidental catalysts gave less interference. Alcohol greatly accelerates the reaction and the diamylphenol and thiophenols used as inhibitors gave smaller effects. The rate constants in the presence of an excess of hydrogen bromide or propene suggest that the equilibrium constant for formation of alkene-halogen acid complex is of the order of 0.3 to 0.5 at 0°.

In the hydrogen bromide–propylene reaction, much less difficulty was encountered with premature reactions at low temperatures, and the meager data at hand indicated that the over-all rate of reaction is very low at −78°, and about two or three times as fast at 30 as at 0°.

Since hexyl bromide is formed in the absence of a solvent, but not in our solvent runs, the formation of hexyl bromide sometimes accompanying the normal addition must be of an order still higher than fourth. This work therefore offers no support for the suggestion of Maass and co-workers[15] that the formation of either 1:1 or 2:1 addition products comes from simple interaction of two alkene–halogen acid complexes.

Summary

A preliminary investigation has been made of the kinetics of the addition of hydrogen bromide to propylene in n-pentane as solvent. A major obstacle was the difficulty in repressing the abnormal addition of hydrogen bromide, even in the presence of inhibitors. The rate of the uncatalyzed normal addition corresponds better to a fourth order reaction, third order with respect to hydrogen bromide, first order with respect to propylene, than to any other integral order. The reaction is accelerated by hydroxylic compounds and then may be of a lower order. The results support the conclusions reached in the study of the hydrogen chloride–isobutylene reaction.

PASSAIC, NEW JERSEY RECEIVED AUGUST 21, 1946

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[9] Kharasch and Mayo, THIS JOURNAL, **55**, 2468 (1933).

[10] Kharasch and Potts, *ibid.*, **58**, 57 (1936).

[11] Walling, Kharasch and Mayo, *ibid.*, **61**, 1711, 2693 (1939).

[12] Mayo and Walling, *Chem. Rev.*, **27**, 351 (1940).

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[14] Ipatieff, Pines and Wackher, *ibid.*, **56**, 2398 (1934).

[15] Coffin, Sutherland and Maass, *Can. J. Research*, **2**, 267 (1930); Brown, Master's Thesis, McGill University (1938).