

### Summary

Selectivity parameter measurements have been made on a series of 2 *M* mixtures of metal bromides and fluorides in HBr and HF. The Lewis acids have been ranked in the order  $\text{AlBr}_3 > \text{GaBr}_3 > \text{TaF}_5 > \text{BBr}_3 > \text{BF}_3, \text{TiF}_4$ , and  $\text{HfF}_4$  in HBr and  $\text{TaF}_5, \text{SbF}_5 > \text{BF}_3 > \text{TiF}_4 > \text{HfF}_4$  in HF. The order is based on the ability of the system to support isomerization relative to proton exchange. It is subject to the unknown effect of comparing homogeneous with heterogeneous systems, and the fact that the selectivity parameter for  $\text{SbF}_5$  and  $\text{TaF}_5$  in HF inverts as the concentration of the Lewis acid increases is an unresolved puzzle.

The Lewis acids tend to exhibit a higher selectivity parameter in HF than in HBr. This is attributed mainly to the enormous difference in dielectric constant and hence dissociative tendencies in the solvents. This overcomes the fact that HBr is more acidic than HF and therefore is a more discriminating rather than a leveling solvent.

The  $(I/E)_{i-C_5}$  scale was found to be related to  $(I/E)_{\text{MCP}}$ , with measurements being compared in different Brønsted acids. This suggests that these scales may provide a basis for comparing the acidity or at least the catalytic activity of Lewis acids in varied media like HBr, HF, and  $\text{HSO}_3\text{F}$ .

The  $I/E$  scale in any one acid appears to correlate with  $H_0$  but since the correlation depends on the solvent one cannot use  $I/E$  to predict  $H_0$  in an unknown solvent or,

*vice versa*, one cannot use  $H_0$  to infer the ion stabilizing properties of the acid.

**Registry No.**—HBr, 11035-10-6;  $\text{AlBr}_3$ , 7727-15-3;  $\text{GaBr}_3$ , 13450-88-9;  $\text{TaF}_5$ , 7783-71-3;  $\text{BBr}_3$ , 10294-33-4;  $\text{TiF}_4$ , 7783-63-3;  $\text{BF}_3$ , 7637-07-2;  $\text{HfF}_4$ , 13709-52-9; HF, 7664-39-3;  $\text{SbF}_5$ , 7783-70-2; HCl, 7647-01-0;  $\text{GaCl}_3$ , 13450-90-3;  $\text{AlCl}_3$ , 7446-70-0;  $\text{BCl}_3$ , 10294-34-5;  $\text{HSO}_3\text{F}$ , 7789-21-1;  $\text{CF}_3\text{SO}_3\text{H}$ ; 1493-13-6;  $\text{NbF}_5$ , 7783-68-8.

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## Solvolytic in Dipolar Aprotic Media.<sup>1</sup> I. Production of Water-Extractable Bromide vs. Olefin Distribution in the Course of the Solvolysis of 2-Bromo-2-methylpentane in Dimethylformamide

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Received December 19, 1973

An investigation about the kinetics of the solvolysis of 2-bromo-2-methylpentane (1) in DMF was conducted using different titration procedures, following distributive extraction between  $\text{CCl}_4$  and water, and gas chromatography. The reaction picture allowed division into distinct phases. The last of these is dominated by an autocatalytic second-order elimination with a notable Saytzeff character (94%) for which kinetic parameters could be estimated. The initial phase shows a remarkable instantaneous release of titrable bromide until a given level is reached; this is attributed largely to the formation of un-ionized species, probably ion pairs. Elimination in this phase has a less pronounced Saytzeff orientation (40–50% terminal olefin) and is thought to be mostly a secondary process, probably succeeding to the formation of a cationic intermediate  $(\text{RDMF})^+$  by solvent substitution. Radiobromide experiments showed a rapid incorporation of  $^{82}\text{Br}$  into a  $\text{CCl}_4$ -extractable form, which was completely inhibited by growing  $\text{C}_{\text{Br}^-}$ , and a slower one which remained unaffected.

Solvolytic in aprotic media of alkyl halides and related compounds, carrying good leaving groups, has, on the whole, received only little attention. With a few exceptions, the scanty data available<sup>2,3</sup> have been obtained in view of an extension of solvent-reactivity correlations. In view of the well-established properties of DAS<sup>4</sup> (substantial ionizing power, high nucleophilicity and basicity, etc.) a more probing investigation was justified.

In 1957 Ross and Labes<sup>3b</sup> determined some first-order rate constants for the hydrogen halide production from *t*-BuCl, dimethylneopentylcarbinyl chloride, and *t*-BuBr in DMF (and *N*-methylpropionamide). Kornblum and Black-

wood<sup>3a</sup> had already noted a halide ion production by several alkyl halides in DMF. Among these was *t*-BuBr, but also there were MeI and benzyl bromide, the latter two being unable to decompose by elimination. In neither study has an elucidation of the elimination or of the salt-forming mechanism been attempted.

In this paper the decomposition of 2-bromo-2-methylpentane (1) in dimethylformamide (DMF;  $\epsilon_{25}$  36.7) is described, as studied by (a) different distributive extraction procedures, using carbon tetrachloride and water, and (b) gas chromatography. Radiobromide incorporation has been followed under comparable conditions.

### Experimental Section

**Materials.** Dimethylformamide (DMF, Fluka Puriss) was dried on Molecular Sieves 4A (Merck) and fractionated *in vacuo* (5 mm) from P<sub>2</sub>O<sub>5</sub> (Merck p.a.), as described by Ritchie and Megerle.<sup>5</sup> A specific conductivity below  $4 \times 10^{-7}$  mho was used as the criterion for the collection (under dry nitrogen) of the usable fractions. 2-Bromo-2-methylpentane (1) was generated (bp 70° (100 mm)) from 2-methyl-2-pentanol and PBr<sub>3</sub> at -20°. The alcohol itself was prepared by Grignard reaction from propyl bromide and acetone. Other reagents were available commercially and purified by standard methods.

**Methods.** Kinetic measurements were made by analyzing aliquots (1–2 ml) taken at appropriate times from the thermostated reaction mixture (usually 65–200 ml), contained in a closed vessel. The crude sampling was done with a syringe through an inert septum, and, after quenching at 0°, a known amount (1 or 2 ml) was withdrawn with a calibrated pipet and transferred to a mixture of 5 ml of CCl<sub>4</sub> and 10 ml water at 0° (method A). After energetic and prolonged shaking, the phases were separated by centrifuging (3000 rpm).

In some experiments the sample was first added to the same amount of CCl<sub>4</sub> and the mixture was stored at 0° for 5 min before extraction with water (method B). This allowed the recombination of some DMF-solvated species that are subject to rapid hydrolysis, but it left unaffected the inorganic bromide which had been formed. Longer residence times did not improve the results. Initially 0.05 M aqueous NaOH was used instead of water, but this was found to be superfluous.

**Titration Procedures.** Both bromide and hydrogen ions were titrated potentiometrically with aqueous AgNO<sub>3</sub> and NaOH. For dilute solutions the end point was established by Gran linearization.<sup>6</sup>

Olefin determinations in the organic layer were sometimes carried out by an adaptation of the method of Colter and Johnson,<sup>7</sup> consisting in the addition of bromine (1 or 2 ml of 0.200 M aqueous KBr–KBrO<sub>3</sub>, 5 ml of acetic acid, and 2 ml of 6 N sulfuric acid per 5-ml sample), conversion of the excess into iodine with aqueous KI (5 ml, 1 N), and titration with 0.1 N thiosulfate after 30 sec. With actual samples from the reaction mixtures, a stable end point could not be obtained, probably due to the presence of unreacted tertiary alkyl bromide. This of course severely limits the quantitative interpretation of these results, as olefin concentrations may have been underestimated by as much as 10–20%. Improvement on the current procedure has not been undertaken, however, as only semiquantitative use was made of these results in confirming a trend established by other means.

**Gas Chromatographic Determinations.** Separation of the olefins was effected on a 6-m column filled with 17% Apiezon L on Gas-Chrom P (80–100 mesh) at 50°, using hydrogen as the eluent. Before the analysis, the sample was fractionated at water-tap vacuum, through a small Vigreux-like column, for 20 sec (when only product distribution was to be determined). To measure olefin yields, cyclohexene was added as an internal standard. In these cases, fractionation had to be prolonged for 3 min to ensure quantitative transfer of the standard. Since this resulted in the distillation of a minor part of the substrate, which was found to show some decomposition on the column, the method could not be confidently used to determine low reaction yields. Before and after the treatment, samples were stored in liquid nitrogen.

**Radiobromide Incorporation.** <sup>82</sup>Br<sup>-</sup> was commercially available from SCK (Mol, Belgium) as an aqueous solution of ammonium bromide. The original solution (4 ml) was evaporated to near dryness (approximately 0.1 ml) and a stock solution was made by addition of 1 ml of DMF. Of this, amounts of 20–100 (exceptionally 500) μl were added to 65 ml of DMF solution in actual experiments. The extra amount of water thus introduced into the reaction medium may be estimated as 30–150 ppm, the lower value being related to the more important results at high specific activity. Total activity amounted to approximately 0.08 μCi/ml in all experiments.

Except for the addition and ultimate assay of radioactive material, the design of the experiments was identical with that of the above kinetic runs followed by distributive extraction between water and CCl<sub>4</sub>.

The samples were counted in a well-type scintillation detector, equipped with a NaI crystal (Tracerlab P-20 C). Corresponding organic and aqueous samples were always counted in immediate succession, thereby obviating the need for corrections for <sup>82</sup>Br decay, as only activity ratios were wanted. These were obtained from the

mean of three determinations after correction for dead time and for volume differences.

Experiments were carried out with substrate concentrations of approximately 0.1 M, with and without addition of NaBr (approximately 0.2 M).

**Treatment of Kinetic Data.** Generally, the reaction picture obtained was too complex to be amenable to kinetic analysis. In some experiments, however, standard kinetic analysis was used to show trends or to estimate some rate constants.

Dominance of autocatalytic reactions was demonstrated by plotting  $\log x/(a - x)$  against time, where  $a$  is the initial substrate concentration and  $x$  is the bromide ion concentration, as calculated from the titration results, which clearly differs<sup>8–10</sup> from the true [Br<sup>-</sup>].

When excess Br<sup>-</sup> is added, the above consideration applies only to a lesser extent. Dissociation of the formed HBr will probably be suppressed to a high degree. Consequently, estimation of  $k_{2,Br^-}$  was here carried out on the basis of pseudo-first-order kinetics, which allowed easy correction for true first-order solvolysis.

The values stated have not been corrected for incomplete dissociation of NaBr. A crude estimate, based on a published value of  $pK_{\text{diss}}$ <sup>11</sup> and a simple Debye–Hückel correction leads to  $\alpha = 0.87$ .

### Results

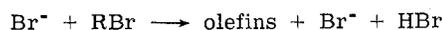
**Reaction Picture.** The reaction has been studied under varying conditions of initial substrate concentration (in the range 0.07–0.5 M) and temperature.

Figure 1 exemplifies the general appearance of the course of solvolysis as followed by bromide titrations (method A) and gc. The notable concurrence of both types of measurements indicates that elimination is the sole net process of the main part of the reaction. The striking variation of the olefin distribution during the reaction, however (Figure 1b), implies that in fact *several different elimination mechanisms are operative*. We found that generally, three consecutive phases could be distinguished: (a) the initial phase, characterized by the occurrence of an almost instantaneous release of titrable bromide followed by a rapid levelling off, manifesting at most a small rise in concentration of the same, and by a rather unexpectedly high, though falling, initial percentage of terminal olefin ( $\geq 50\%$  2-methyl-1-pentene); (b) a phase of transition, where bromide production appears to be resumed and which may include a first-order elimination as the major feature, with a regiospecificity of approximately 40% 1-olefin; (c) the autocatalytic phase, where the data are reasonably well amenable to treatment by autocatalytic kinetics. In this last case a pronounced Saytzeff orientation is noted.

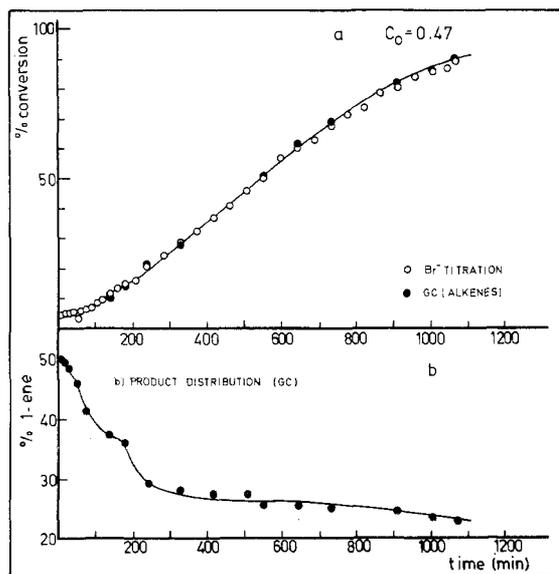
**The Autocatalytic Elimination (Phase c).** In view of the now well-known basicity of halide ions in aprotic media, limiting E2-type eliminations, caused by Br<sup>-</sup>, and most probably HBr<sub>2</sub><sup>-</sup>, too, are not unexpected, as these ions are generated in the solution. Comparable reactions have recently been studied<sup>12</sup> and were identified as E2C, as designated by Winstein, Parker, and their coworkers.<sup>12a</sup>

At a  $C_{0,\text{substr}}$  of approximately 0.46 M our present data are reasonably well in agreement with autocatalytic kinetics from 25 to 90% conversion at 30 and at 45° and from 45 to 90% at 60°. In fact, perfect agreement is not likely because of the fact that the titration results are not really proportional to  $C_{Br^-}$  and because of the expected importance of HBr<sub>2</sub><sup>-</sup> ions and the attendant elimination reaction.

Estimates for  $k_{E2,30}$  of the reaction



have been obtained, by use of method A and H<sup>+</sup> titration, the reaction mixture containing, besides 1 ( $C_0 \approx 0.1$  M), also NaBr ( $C_0 \approx 0.1$ – $0.2$  M). The estimated mean of  $3.8 \times 10^{-4} \text{ sec}^{-1} \text{ mol}^{-1}$  compares well with the rate constant of related E2C reactions of halide ions in DMF and acetone.<sup>12b,13</sup> It is in accord also with the apparent rate con-



**Figure 1.** (a) Course of solvolysis of 1 ( $C_0 = 0.47 M$ ) in DMF at  $30.0^\circ$ , as measured by bromide titration and gc (olefin determinations). (b) Attendent olefin distribution (gc).

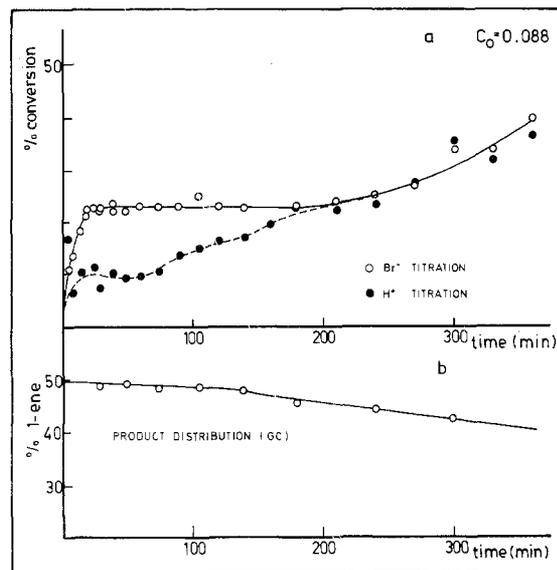
stant  $k_{E2,app,30} = 1.4 \times 10^{-4} \text{ sec}^{-1} \text{ mol}^{-1}$  for the autocatalytic phase of solvolysis ( $C_{0,1} = 0.46 M$ ), taking into account incomplete dissociation of HBr etc. Addition of  $10^{-2} M$  picric acid does not affect the reaction rate.

The regiospecificity for this phase was determined by adding an even more substantial amount of NaBr ( $C_{NaBr} \approx 0.5 M$ ,  $C_1 = 0.1 M$ ). An essentially constant product orientation of  $16.1 \pm 0.5\%$  1-olefin was obtained over the whole course of reaction (and was equally unaltered by addition of  $10^{-2} M$  picric acid).

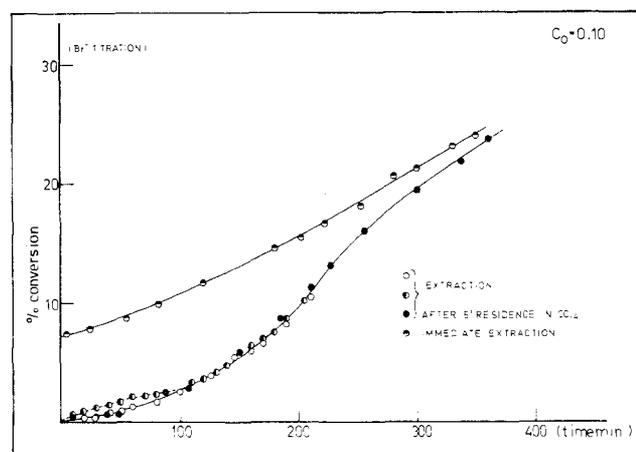
Conceivably, when smaller substrate concentrations (e.g., of the order of  $0.1 M$ ) are used, the relative importance of the autocatalytic part of the reaction in solvolysis is decreased and its dominance is postponed. These conditions evidently are more convenient for the study of the genuine solvolytic phenomena.

**The Initial Phase (Phase a).** This part of the reaction picture offers some rather unusual features; viz., an immediate and fast rise of titrated bromide, suddenly followed by a very marked leveling off (Figure 2a). This aspect is most readily observed at lower temperatures, e.g.,  $30^\circ$ . In the experiments at  $45^\circ$  its occurrence is reduced to a "shoulder" and can only be conjectured at  $60^\circ$ . The use of substrate concentrations in a range of  $0.07\text{--}0.1 M$  allows the observation of an almost constant level of apparent  $C_{Br^-}$ , for more than 200 min (!) as evidenced by Figure 2a. Under these conditions, this steady-state  $C_{Br^-}$  amounts to more than 20% of the total bromide, although its absolute value remains of the order of  $0.02\text{--}0.025 M$  in all experiments. However unusual, these results stand not alone in the literature. Winstein, *et al.*,<sup>14</sup> gave a cursory description of an analogous albeit less pronounced phenomenon, observed after dissolving *t*-BuBr in acetone, however, without explanation. The similarity of the substrate and the dipolar aprotic character of the solvent induce us to believe that in these media this behavior is of some generality.

On the supposition that acid production itself could in any way have brought about the leveling off, picric acid was added, which at the concentration used ( $10^{-2} M$ ), is completely dissociated.<sup>9</sup> In fact, the image of the experiment is greatly changed. Bromide titration now shows a slow, linear increase, although still starting at a level of  $0.007 M$  which



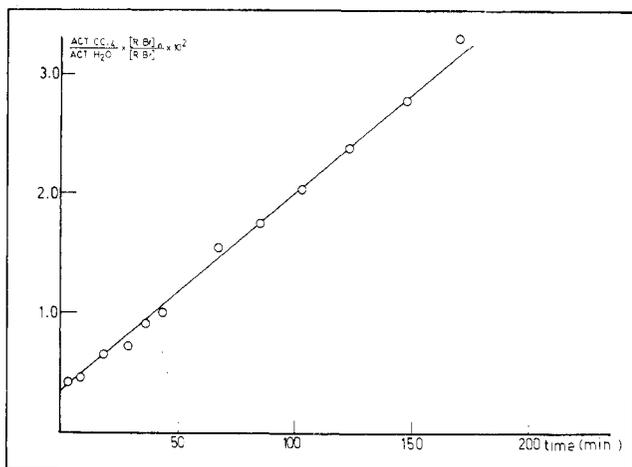
**Figure 2.** (a) Course of solvolysis of 1 ( $C_0 = 0.088 M$ ) in DMF at  $30.0^\circ$ , as measured by  $Br^-$  and  $H^+$  titration. (b) Attendent olefin distribution (gc).



**Figure 3.** Course of solvolysis of 1 ( $C_0 = 0.10 M$ ) in DMF at  $30.0^\circ$ , in the presence of  $0.01 M$  picric acid. The lower curve represents results obtained by method B (5-min residence time in  $CCl_4$ , prior to water extraction); the upper curve represents results obtained by method A (immediate distributive extraction with a water- $CCl_4$  mixture).

seems to have been formed instantaneously, right at the start of the solvolysis. The lowering (from 22 to 7%) is more suggestive for a salt effect than for inhibitory action.

A refined extraction method was then devised (method B) whereby the samples were given a residence time of 5 min in  $CCl_4$  before extraction with water. Figure 3 (lower curves) establishes that the instantaneous release of titratable bromide is due, not to HBr or its ionization products, but to some species able to recombine in a medium of low ionizing power while being subjected, on the other hand, to immediate hydrolysis during water extraction. It would appear to us that some kind of ion pair is the species most likely to display this behavior. In the course of the reaction, part of the recombinable bromide may well be present as free ions, provided a cationic solvolysis product is formed simultaneously. The lower curve may then be identified with the total elimination. Its sigmoidal shape and the low initial rate suggest that, at least in this phase of the reaction, the elimination consists largely, if not wholly, of a secondary process. The important primary process may then be thought of as a first-order substitution by the solvent to



**Figure 4.** Incorporation of added  $^{82}\text{Br}^-$  into a  $\text{CCl}_4$ -extractable form during  $\text{Br}^-$ -induced E2 elimination of 1 in DMF at  $30.0^\circ$  ( $C_0 = 0.097\text{ M}$ ;  $C_{\text{NaBr}} = 0.207\text{ M}$ ; approximately  $0.08\text{ }\mu\text{Ci } ^{82}\text{Br}/\text{ml}$ ). Relative activities of  $\text{CCl}_4$  and water layers after distributive extraction were corrected, as shown, for substrate decomposition.

yield a cationic intermediate of probable structure  $\text{RDMF}^+$  (2)<sup>15-18</sup>



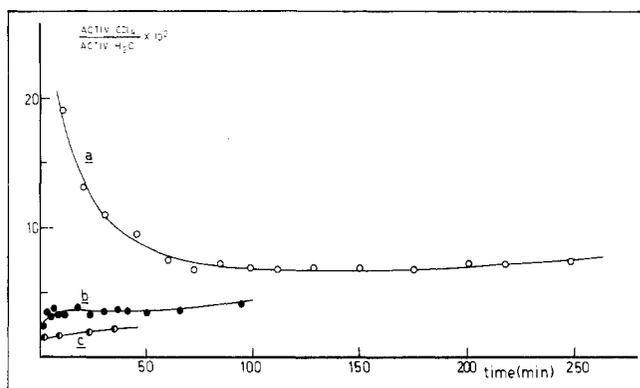
This is in accordance with the observation of Kornblum and Blackwood<sup>3d</sup> that halide ion was liberated from methyl iodide and from benzyl bromide in DMF.

In fact, several of our own experiments demonstrate that acid and olefin production are lagging behind bromide formation. In a consistent manner, titration for  $\text{Br}^-$  gave higher results than acid determinations. Figure 2a shows an outstanding example. Olefin titrations, though less quantitative, confirm these data. Noteworthy is the fact that, in all cases studied, the resuming of apparent bromide production coincided with the disappearance of any appreciable difference in analysis results.

Olefin distribution of this phase is shown in Figure 2b. Starting at approximately 50% 1-ene, this value is slowly lowered to 46% 1-ene at the end of the phase. By comparable determinations with  $10^{-2}\text{ M}$  picric acid added ( $C_{0,\text{substr}} = 0.096\text{ M}$ ), an essentially constant amount of 41% ( $41.1 \pm 0.8\%$ ) was found. This value may be attributed reasonably well to the elimination of intermediate 2. The true regio-specificity may be somewhat higher still, as even here a contribution of the autocatalytic  $\text{Br}^-$ -induced elimination is to be expected.<sup>19</sup> The initial product orientation in absence of any addition suggests that at the very start of the solvolysis still another elimination mechanism could be operative, endowed with a regio-specificity close to Hofmann direction! This characteristic probably excludes a straightforward  $\text{E1}^{20,21}$  mechanism, which moreover would not be inhibited by increase of acid concentration or of ionic strength.

To our knowledge the only previous record of a product distribution attending solvolytic elimination in a dipolar aprotic solvent was made by Parker and coworkers, who noted 50% 1-ene for the elimination of *tert*-pentyl bromide in acetone at  $50^\circ$ .<sup>22</sup>

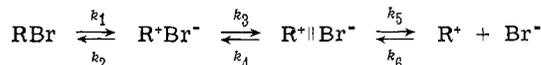
**The Intermediate Region.** In view of the foregoing discussion it is doubtful that this region should be considered as a phase with proper identity. Indeed, it is more likely that the apparent resuming of bromide production is nothing but the visible continuation of a process which was previously concealed by the superposition of the initially high level of ion-pair concentration. This interpretation is corro-



**Figure 5.** Incorporation of added  $^{82}\text{Br}^-$  (approximately  $0.08\text{ }\mu\text{Ci}/\text{ml}$ ) into a  $\text{CCl}_4$ -extractable form, during solvolysis of 1 ( $C_0 = 0.080\text{ M}$ ) in DMF at  $30.0^\circ$ . Indicated are the relative activities of the layers after distributive extraction, with  $\text{CCl}_4$  and water, of solvolysis samples. Total activity added per volume was almost equal, but, due to decay, "chemical" concentration of added  $\text{Br}^-$  was approximately  $2 \times 10^{-7}\text{ M}$  (a),  $1 \times 10^{-6}\text{ M}$  (b), and  $5 \times 10^{-6}\text{ M}$  (c) in successive experiments.

borated by fitting of the data of Figure 1 to first-order kinetics. In a  $\log(a-x)$  vs.  $t$  plot this "phase" is well approximated by a straight line, which after extrapolation intersects with the ordinate at a value only slightly above  $\log a$ .<sup>23</sup>

**Radiobromide Incorporation Experiments.** We have performed some experiments in order to examine the incorporation of radiobromide into a form which is to be found in the  $\text{CCl}_4$  phase after distributive extraction with  $\text{CCl}_4$  and water of solvolysing DMF samples. The peculiar results, shown in Figure 5, may be used to shed some light on the possible pathways of solvolysis. A tentative explanation may be offered on the basis of the well-known Winstein ionization scheme<sup>24</sup>



In contrast to the situation in most protic media, recombination of the dissociated ions ( $k_6$ ) may well be a very fast reaction, owing to the enhanced nucleophilicity of halide ions.<sup>4a,b</sup> This should allow a rapid incorporation of  $^{82}\text{Br}^-$ , especially if  $k_4$  is not too small. Unhindered continuation of this process, however, would bring the major part of the activity in a  $\text{CCl}_4$ -extractable form after a short time, and this is not the case. If, however, the original quasiequilibrium value of carbenium ion concentration is very small, as can be postulated reasonably ( $k_6$  large!), the progress of solvolysis and the production of  $\text{Br}^-$  by an independent way will soon inhibit radiobromide incorporation automatically. Indeed, if a quasiequilibrium between the components of the Winstein scheme is assumed, it follows that  $[\text{R}^+] = k_5[\text{R}^+\|\text{Br}^-]/k_6[\text{Br}^-] \approx [\text{RBr}]/[\text{Br}^-]$ .

The rate of incorporation of  $^{82}\text{Br}^-$  is then proportional to  $[\text{RBr}][^{82}\text{Br}^-]/[\text{Br}^-]$  or roughly to  $1/[\text{Br}^-]$ . This is in accord with the much lower initial incorporation rates, in case radiobromide of lower specific activity was used (Figure 5b and c) as this corresponded to a higher "chemical" bromide concentration.

Radiobromide addition to solvolysis mixtures (Figure 5) also discloses a more gradual incorporation at a lower rate, independent of the exceptional uptake at high specific activity and uninhibited by the growing bromide concentration. Even in reaction mixtures with  $0.2\text{ M}$   $\text{NaBr}$  present, the incorporation of  $^{82}\text{Br}^-$  is nearly linear with time, after correction for the decreasing substrate concentration (Fig-

ure 4). These results may be explained by the occurrence of some sort of exchange reaction at the level of, *e.g.*, the solvent-separated ion pair. In fact, the concentration of any ion pair can be expected to be proportional to that of the substrate and the  $^{82}\text{Br}^-$  activity in the water soluble form remains almost at a constant level for the duration of the experiment.

### Summary and Conclusions

We believe to have demonstrated unambiguously that the main initial solvolysis product of 2-bromo-2-methylpentane in DMF consists of a cationic substitution product  $\text{RDMF}^+$  (2), which consequently is eliminated to yield 2-methylpentenes with a regioselectivity of more than 40% terminal olefin (25% Hofmann elimination if corrected for statistical factors). In the course of solvolysis, the autocatalytic second-order eliminations, with  $\text{Br}^-$  and probably  $\text{HBr}_2^-$  as basic reagents, become the dominant reactions, at least in the concentration range studied. In accord with work on related reactions a pronounced Saytzeff orientation is found (94% including correction for statistical factors).

At low ionic strength the existence of yet another elimination mechanism is suspected.

The first phase of solvolysis is attended by the rapid formation of appreciable quantities of water-extractable species, the major part of which is tentatively identified as ion pairs. As none of the classical procedures used allows the determination of total solvolysis (*i.e.*, elimination plus substitution), no clear distinction can be made between these and  $\text{RDMF}^+$  (2), whose formation may also be readily reversible during its stay in  $\text{CCl}_4$  solution (procedure B).

$^{82}\text{Br}$  experiments indicate, among other things, that ionization and dissociation reactions in the system studied were fast and reversible to a great extent.

Registry No.—1, 4283-80-1.

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