

dissolved olefin is considerably smaller, and operates in a direction opposite to that produced by the changes in the activity coefficients of the ionic substances. There is a considerable presumption that the medium effect arises predominantly from a change with acid concentration of the energy of activation since the observed energy is  $0.56 \pm 0.18$  kcal. lower for the 0.973 *m* acid than for the 0.0909 *m* acid.

A single experiment was made at 45° on the rate of pressure drop in a system composed of gaseous isobutene and a solution containing 0.0909 *m* nitric acid and 0.88 *m* potassium nitrate, at a value of the volume ratio *r* where an approximate estimation

of the value of *h* sufficed to yield a value of  $k_p$  which should not be in error by more than 5%. The ratio of this value of  $k_p$  to that in 0.0909 *m* acid without the salt was 1.37. This implies that the effect of added potassium nitrate on the quantity  $\gamma_{H^+}/\gamma_{\pm}$  is materially smaller than the effect of the same amount of additional nitric acid. The close equivalence of the effects of added acid and salt on the values of  $k_c/[\text{OH}_3^+]$  which Lucas and Ebertz observed must depend therefore upon a compensation in which the different effects of acid and salt on  $\gamma_{H^+}/\gamma_{\pm}$  are cancelled by different effects of acid and salt on  $\gamma_0$ .

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## The Vapor Phase Reaction between Phosgene and Alcohols

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The vapor-phase reaction between phosgene and alcohols has been demonstrated. With an excess of phosgene, the principal products from primary and secondary alcohols were the corresponding chloroformates. In one experiment with an excess of *n*-propyl alcohol, the carbonate was obtained in good yield. *t*-Amyl alcohol was converted principally to *t*-amyl chloride. Small amounts of alkyl chloride and olefin were formed in a number of the experiments.

Although the liquid-phase reactions of phosgene have been widely investigated, the reactions of that compound in the vapor-phase are relatively unexplored. The gas-phase preparation of isocyanates and carbamyl chlorides in high yields from amines<sup>1</sup> suggested similar reactions with other active hydrogen compounds, such as alcohols, which are reported here.

It is well known that alkyl chloroformates decompose in the gas phase to give the corresponding olefin, alkyl chloride, carbon dioxide and hydrogen chloride.<sup>2</sup> For example, the half-life of isobutyl chloroformate has been reported to be one hundred and sixty minutes at 267°, sixteen at 302°.<sup>3</sup> Furthermore, it is considered possible that phosgene and an alcohol could react in such a way as to give directly an olefin and an alkyl chloride, without the intermediate formation of a chloroformate. Consequently the products expected from this study included all of the above mentioned compounds. The reaction was investigated primarily with the object of preparing substituted chloroformates, however.

By using sojourn times of the order of three seconds and temperatures of 100–250°, 50–80% yields of chloroformates were obtained from primary alcohols, methyl through octyl. A 69% yield of propyl carbonate also was realized. Isopropyl and cyclohexyl alcohols gave 55 and 73% of the chloroformates, respectively. *t*-Amyl alcohol, however, did not react completely, and was converted to the chloroformate in only 7% yield, isolated as the urethan. Cyclohexyl and octyl chloroformates were also converted to the urethans. Phenol was recovered unchanged, even when temperatures as high as 430° were used. It is possible that the phe-

nol would have reacted at much longer sojourn times, however.

In many of the experiments small amounts of olefin and alkyl chloride were obtained. The data did not show conclusively that these products were formed in the vapor-phase; they may have been the result of decomposition during standing or distillation.

It was demonstrated conclusively that the reaction between methanol and phosgene at 85–100° took place in the vapor-phase reactor. Treatment of the crude product with phenyl isocyanate gave no methyl carbanilate, showing the absence of unreacted methanol in the crude chloroformate. The yield of chloroformate was 73%. On the other hand, methanol saturated with phosgene at 10–15° and treated with phenyl isocyanate as before gave 61% of methyl carbanilate and only 13% of the chloroformate.

### Experimental

**General Method.**—The apparatus and procedure were essentially the same as those described for the vapor-phase reaction between amines and phosgene,<sup>1</sup> with the following modifications. The thermowell in the reactor extended to within 1 in. of the tip of the phosgene inlet tube so that the temperature could be measured at any point in the reaction zone. An iron-constantan thermocouple was used for this measurement. The reaction zone had a volume of 95 cc., and feed rates were such that sojourn times of 3–4 sec. were obtained. The phosgene:alcohol molar ratio was 1.1–2.0 in all cases except in the preparation of propyl carbonate. The receiver was cooled in an ice-water-bath. The best yields and corresponding temperatures are shown in Table I.

The temperatures listed are those observed at the point of mixing of phosgene and alcohol. The temperature farther up the reactor was generally 10–20° higher. All yields are based on the alcohol. All additional information is given in Table II or under the heading of the alcohol used.

**Preparation of Urethans.**—To obtain a check on the yields achieved by distillation (Table I), certain of the above experiments were repeated and the crude product was converted to the urethan, as follows. An equal volume of isohexane was added to the crude condensate. Concentrated aqueous ammonia (sp. gr. 0.90) was added with stirring, at

(1) R. J. Slocombe, E. E. Hardy, J. H. Saunders and R. L. Jenkins, *THIS JOURNAL*, **72**, 1888 (1950).

(2) A. R. Choppin and E. L. Compere, *ibid.*, **70**, 3797 (1948).

(3) L. T. Lessig, *J. Phys. Chem.*, **36**, 2325 (1932).

TABLE I

| PREPARATION AND PROPERTIES OF CHLOROFORMATE |            |          |           |             |
|---|------------|----------|-----------|-------------|
| Alcohol used                                | Temp., °C. | Yield, % | B.p., °C. | Press., mm. |
| Methyl <sup>a</sup>                         | 85         | 68       | 69-72     | 750         |
| Ethyl <sup>a</sup>                          | 115        | 66       | 89-91     | 750         |
| <i>n</i> -Propyl <sup>a</sup>               | 160-165    | 71       | 113-116   | 750         |
| Isopropyl <sup>a</sup>                      | 150        | 55       | 57-58     | 145-150     |
| <i>n</i> -Amyl <sup>b</sup>                 | 180-190    | 80       | 68-70     | 25-28       |
| <i>t</i> -Amyl <sup>c</sup>                 | 150-160    | 0        | .....     | .....       |
| Cyclohexyl <sup>d</sup>                     | 175-185    | 73       | 38-44     | 2           |
| <i>n</i> -Octyl <sup>e</sup>                | 200-205    | 54       | 119-123   | 30          |
| Phenol                                      | 200-430    | 0        | .....     | .....       |

<sup>a</sup> C. S. Hamilton and C. Sly, *THIS JOURNAL*, **47**, 435 (1925). <sup>b</sup> K. W. F. Kohrausch and R. Sabathy, *Monatsh.*, **72**, 303 (1939);  $n_D^{20}$  1.4175,  $d_{25}^{25}$  1.020; calcd., Cl, 23.55; found, Cl, 22.90, 23.20. <sup>c</sup> E. Merck, German Patent 254,471, *Chem. Zentr.*, **84**, I, 346 (1913), reported that this compound decomposed at room temperature, could not be distilled. <sup>d</sup> M. E. Fourneau, M. Montaigne, and J. Puyal, *Anales. soc. espan. fis. quim.*, **18**, 323 (1920); *cf. C. A.*, **16**, 239 (1922);  $n_D^{20}$  1.4587,  $d_{25}^{25}$  1.122; calcd., Cl, 21.81; found, Cl, 21.60. <sup>e</sup> P. Carre, *Bull. soc. chim.*, [5] **3**, 1064 (1936);  $n_D^{20}$  1.4308,  $d_{25}^{25}$  0.978; calcd., Cl, 18.40; found, Cl, 18.26.<sup>4</sup>

TABLE II

| PREPARATION OF URETHANS      |          |             |                          |       |
|------------------------------|----------|-------------|--------------------------|-------|
| Alcohol used                 | Yield, % | M.p., °C.   | Nitrogen, % <sup>4</sup> |       |
|                              |          |             | Calcd.                   | Found |
| <i>t</i> -Amyl <sup>a</sup>  | 7        | 94-95       | 10.68                    | 10.35 |
| Cyclohexyl <sup>b</sup>      | 52       | 111.3-112.3 | 9.79                     | 9.46  |
| <i>n</i> -Octyl <sup>c</sup> | 45       | 68-68.5     | 8.09                     | 7.90  |

<sup>a</sup> E. Merck, German Patent 254,472, *Chem. Zentr.*, **84**, I, 346 (1913). <sup>b</sup> Reference (d), Table I. <sup>c</sup> R. A. Jacobson, *THIS JOURNAL*, **60**, 1742 (1938).

5-20°, until no more heat was evolved. The mixture was filtered. The solid was triturated with methanol to dissolve the urethan, which was recrystallized. The isohexane layer was distilled to isolate any olefin or alkyl chloride. The residue from this distillation was either chloroformate or urethan. If chloroformate, the residue was converted to the urethan as before. The yields of urethan, and hence minimum yields of chloroformate, are shown in Table II. All melting points are corrected. The lower yields in Table I, compared to Table I, are probably due to crystallization losses.

**Methanol.**—du Pont methanol, 99.85% minimum purity,  $n_D^{20}$  1.3284, was used. An unequivocal demonstration that the reaction between methanol and phosgene took place in the vapor-phase reactor was desired. The possibility that methanol could have passed through the reactor unchanged, and then reacted with dissolved phosgene in the receiver was considered.

Eighty grams (2.5 moles) of methanol was treated with an excess of phosgene at 85°, in the usual way. Two hours was required to complete the reaction. The condensate was maintained at 10-20° while 300 g. (2.5 moles) of phenyl isocyanate was added. The resulting mixture was distilled to give 172 g., 73%, of methyl chloroformate, b.p. 70°, and

(4) The authors wish to thank Messrs. F. A. Barker, W. B. Dunlap, F. R. Heifner and R. L. Tate for these analyses.

288 g., 96%, of phenyl isocyanate, b.p. 96° (90 mm.). The liquid residue weighed about 10 g. No urethan was obtained. This experiment demonstrated that at the end of the phosgene-alcohol reaction there was less than 4% of unreacted methanol in the crude condensate.

The following experiment was performed to show that the above 73% yield of chloroformate was not the result of a very rapid reaction between condensed methanol and phosgene in the receiver. Eighty grams of methanol was saturated with phosgene during two hours at 10-15°. As before, 300 g. of phenyl isocyanate was added. The resulting mixture, which solidified, was diluted with 400 cc. of toluene and was distilled through a 14-in. helix-packed column. The following fractions were collected: (1) 31.5 g. (13%) of methyl chloroformate, b.p. 70-72°, (2) 67 g. of intermediate, b.p. 77-110°, (3) 277 g. of toluene, (4) 78.5 g. (26%) of phenyl isocyanate, b.p. 40° (5 mm.), and (5) 230 g. (61%) of residue, impure methyl carbanilate, m.p. 38-40°. The residue after recrystallization from *n*-hexane melted at 46.5-47.5°. These results demonstrated that at least the major portion of the previous reaction took place in the vapor-phase reactor.

***n*-Propanol.**—Propyl carbonate was also prepared in 69% yield when a temperature of 180-200° and a phosgene:alcohol ratio of 0.26 were used. The product boiled at 167-168°.<sup>6</sup>

***t*-Amyl Alcohol.**—*t*-Amyl alcohol was obtained from the Sharples Chemical Company and redistilled, b.p. 102-102.5°,  $n_D^{20}$  1.4032.

The product from 100 g. of alcohol weighed 100 g., boiled at 43-78°, and contained 7 cc. of water. Redistillation gave 3 g. (3.8%) of impure isopentene, b.p. 38-46°,  $n_D^{20}$  1.3856-1.3876,<sup>7</sup> and 73.3 g. (60.5%) of *t*-amyl chloride, b.p. 83-85°,  $n_D^{20}$  1.4045-1.4088.<sup>8</sup> No chloroformate was found.

The experiment was repeated with 300 cc. of toluene in the receiver. The crude product was treated as described under the preparation of urethans, except that isohexane was not used. Distillation gave 44 g. (47%) of crude *t*-amyl chloride, b.p. 65-90°,  $n_D^{20}$  1.4072, and 49 g. of unreacted alcohol containing some toluene. Based on the index of refraction of the pure alcohol and that of the toluene used (1.4925), the alcohol fraction was 69% pure, giving a 33 g. (33%) recovery of alcohol.

These results indicated that all of the alcohol did not react in the vapor phase. Apparently on distillation in the presence of phosgene unreacted alcohol was converted to the chloride. This assumption was confirmed by saturating 35 g. of *t*-amyl alcohol with phosgene and hydrogen chloride at 10-20°. Distillation as before gave 33.5 g. (79%) of *t*-amyl chloride, b.p. 77-84°,  $n_D^{20}$  1.4040.

The crude *t*-amylurethan, isolated from isohexane as described earlier, melted at 86-88°. Recrystallization from isohexane gave the results shown in Table II. Recrystallization from methanol, however, gave a compound melting at 69.5-71.5°. The analysis<sup>4</sup> indicated that this was the alcoholate, calcd. for  $C_5H_{11}OCONH_2 \cdot CH_2OH$ : N, 8.58. Found: N, 8.57.

**Phenol.**—Fifty grams of phenol was treated with phosgene in the usual way at 200-230°. The only compound recovered was phenol, 43 g., 86%. The reaction was repeated at 320-340° and at 390-430°, with the same results.

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