

(c) *Determination of Isomer Distribution in the Benzoylation of Toluene*

The monobenzoylation of toluene was carried out by procedures identical with those used in the kinetic studies on benzene. The isomeric products were separated from the reaction solution by Procedure A of Brown and Jensen⁸ and their relative proportions were determined by gas chromatography using Carbowax 1500 at 140° as the stationary phase. Artificial mixtures of *ortho*-, *meta*-, and *para*-methylbenzophenones were prepared and analysed on the same chromatograph to identify the individual components and determine the response of the detector to each.

(d) *Melting Behaviour of Benzoyl Chloride under Pressure*

In high pressure kinetic experiments it is important to ensure that none of the components of the reaction mixture freezes or forms a separate phase under compression. To that end we carried out freezing point measurements on the solvent, benzoyl chloride, and its mixtures with 0.5 mole/l. aluminium chloride and 0.5 mole/l. benzene. The results for pure benzoyl chloride are:

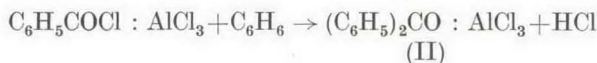
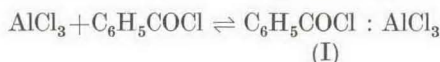
| | | | | | |
|----------------------|-------|--------|--------|--------|--------|
| pressure (atm) | 1 | 1160 | 1375 | 1680 | 1945 |
| freezing temperature | -0.5° | +19.7° | +24.0° | +30.9° | +37.0° |

Although the freezing pressure was slightly raised by the presence of dissolved aluminium chloride and benzene, we nevertheless deemed it safest to limit our upper working pressure to 1500 atm at 29.6°.

RESULTS

(a) *Kinetics*

The stoichiometry of the benzoylation of benzene, catalysed by aluminium chloride in benzoyl chloride solution, can be expressed by the equations³



Initially the aluminium chloride is present in the form of the addition complex (I) but as the reaction proceeds it preferentially forms an inactive complex (II) with benzophenone. Even in an excess of benzoyl chloride and benzene the reaction effectively stops when all the aluminium chloride has been consumed in this way.³

Brown and Jensen³ showed that, at atmospheric pressure, the reaction follows second-order kinetics:

$$\text{rate} = \frac{d[(\text{C}_6\text{H}_5)_2\text{CO} : \text{AlCl}_3]}{dt} = k[\text{C}_6\text{H}_5\text{COCl} : \text{AlCl}_3][\text{C}_6\text{H}_6]$$

and we have confirmed that the same kinetics hold at high pressures. The results for two typical runs are listed in Table I and the general results are summarized in Table 2. The rate constant at atmospheric pressure is within 10% of that found by Brown and Jensen.

Although the results show some scatter, it is clear that the reaction is accelerated by raising the pressure. Applying the quasi-thermodynamic relation:⁹

$$-RT \frac{\partial \ln k}{\partial P} = \Delta V^\ddagger$$

⁸ Brown, H. C., and Jensen, F. R., *J. Am. Chem. Soc.*, 1958, **80**, 2296.

⁹ Evans, M. G., and Polanyi, M., *Trans. Faraday Soc.*, 1935, **31**, 885.

TABLE 1
RATE DATA FOR THE BENZOYLATION OF BENZENE AT 29.6°
Initial concentrations (mole fractions): $[C_6H_6] = 0.058$,
 $[C_6H_5COCl : AlCl_3] = 0.035$

| Time (min) | 1 Atm | | Time (min) | 1000 Atm | |
|---------------|------------------------|--|---------------|------------------------|--|
| | Percentage Reaction | 10^4k (mole-fraction ⁻¹ sec ⁻¹) | | Percentage Reaction | 10^4k (mole-fraction ⁻¹ sec ⁻¹) |
| 48 | 10.3 | 6.6 | 51 | 11.9 | 7.5 |
| 100 | 14.9 | 5.0 | 100 | 25.7 | 9.3 |
| 158 | 22.9 | 5.1 | 150 | 35.7 | 9.6 |
| 200 | 31.7 | 6.1 | 238 | 47.1 | 9.2 |
| 275 | 36.0 | 5.3 | 300 | 50.8 | 8.3 |
| 350 | 42.6 | 5.3 | 350 | 55.1 | 8.2 |
| 400 | 48.9 | 5.8 | 400 | 59.7 | 8.3 |
| 452 | 49.7 | 5.3 | 450 | 64.6 | 8.7 |
| 500 | 53.7 | 5.7 | 500 | 64.6 | 7.9 |
| | | Av.: 5.6 | | | Av.: 8.6 |

TABLE 2
EFFECT OF PRESSURE ON THE RATE CONSTANT FOR BENZOYLATION
OF BENZENE AT 29.6°

| Initial Concentrations (mole fractions) | | Pressure (atm) | 10^4k (mole-fraction ⁻¹ sec ⁻¹) |
|--|-------------------------|-------------------|--|
| $[C_6H_6]$ | $[C_6H_5COCl : AlCl_3]$ | | |
| 0.086 | 0.037 | 1 | 6.2 |
| 0.058 | 0.035 | 1 | 5.6 |
| 0.047 | 0.102 | 1 | 5.3 |
| 0.055 | 0.050 | 1 | 5.8 |
| 0.104 | 0.050 | 1 | 5.8 |
| | | | Av.: 5.7 |
| 0.086 | 0.037 | 1000 | 9.9 |
| 0.058 | 0.035 | 1000 | 8.3 |
| 0.047 | 0.102 | 1000 | 8.6 |
| 0.055 | 0.050 | 1000 | 8.3 |
| | | | Av.: 8.8 |
| 0.058 | 0.035 | 1500 | 11.7 |
| 0.047 | 0.102 | 1500 | 12.2 |
| 0.055 | 0.050 | 1500 | 12.2 |
| 0.045 | 0.036 | 1500 | 13.1 |
| | | | Av.: 12.3 |