we find that the pressure effect corresponds to a volume of activation $\Delta V^{\ddagger} = -11\cdot4\pm$ 1 cm^3 mole^{-1}.

(b) Isomer Distribution Ratios

Table 3 (p. 1916) lists the results of 11 separate measurements of the relative yields of methyl benzophenones formed by benzoylating toluene under the conditions described in the Experimental section.

The isomer ratios were very close to those found by Brown and Jensen,[8] and were not measurably altered by increasing the pressure.

DISCUSSION

(a) Kinetics

Although the exact mechanism of Friedel–Crafts benzoylations is not known with certainty,[4] it is probable that the present reaction proceeds by the following steps:
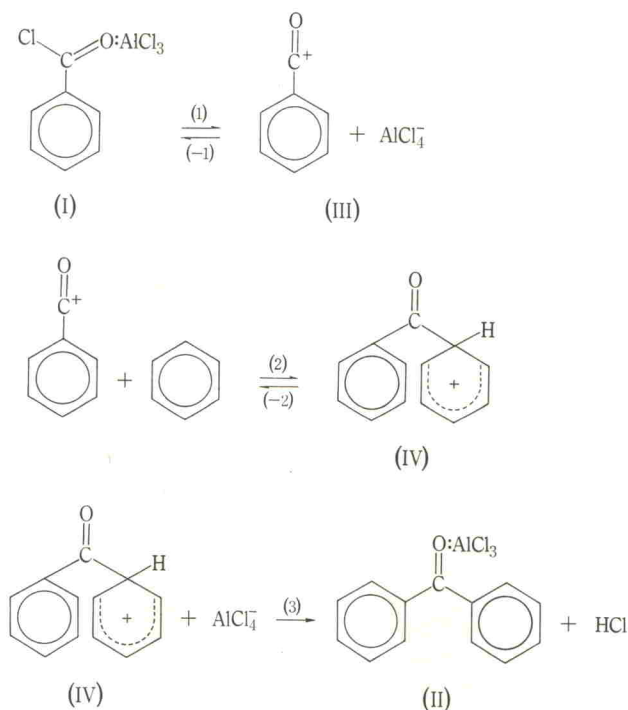
This mechanism would give the observed second-order kinetics if (3) were the rate-determining step, or if the ions (III) existed mainly as ion pairs and (2) were the rate-determining step. The second alternative is the more likely, since it is known that the rate of benzoylation of hexadeuterobenzene[4] is not very different from that of benzene; if (3) were the slow step the kinetics would show a marked isotope effect.

Evidence of the prereaction equilibrium (1) is to be found in the extremely fast exchange of chloride ions between benzoyl chloride and aluminium chloride[10] and the fact that mixtures of Friedel–Crafts catalysts with benzoyl chloride are electrolytic conductors.[11] However, the concentration of the ionized form must be small, since Susz *et al.*[12] were unable to detect it by infrared methods that have shown the presence, in analogous mixtures, of $CH_3CO^+AlCl_4^-$ [13] and $C_6H_5CO^+SbF_6^-$.[14]

TABLE 3

DISTRIBUTION OF ISOMERIC METHYL BENZOPHENONES FORMED BY BENZOYLATING TOLUENE

Pressure (atm)	Isomer Distributions (%)		
	ortho	*meta*	*para*
1	9·5	1·5	89·0
1	10·1	1·9	88·0
1	9·6	1·2	89·2
1	9·2	1·5	89·3
500	8·6	1·6	89·8
500	12·2	1·4	86·2
1000	9·8	2·2	88·7
1000	8·9	2·0	89·1
1500	9·6	1·7	88·7
1500	8·5	1·9	89·6
1500	9·2	2·7	89·1

If the postulated mechanism is correct, the effect of pressure on the measured rate constant k must depend on changes in both the equilibrium constant $K_1(= k_1/k_{-1})$ and the rate constant k_2. In fact $\Delta V^\ddagger$ must be a composite quantity:

$$\Delta V^\ddagger = -\mathbf{R}T\frac{\partial \ln k}{\partial P} = -\mathbf{R}T\frac{\partial \ln (K_1 k_2)}{\partial P}$$
$$= \Delta \bar{V}_1 + \Delta V_2^\ddagger$$

where $\Delta \bar{V}_1$ denotes the change of partial molar volumes for the ionization reaction (1) and $\Delta V_2^\ddagger$ is the activation volume for reaction (2). The kinetic data alone offer no means of separating the two contributions and there is at present no direct way of measuring K_1 and hence $\Delta \bar{V}_1$. But from theoretical arguments and from the known

[10] Oulevey, G., and Susz, B. P., *Helv. Chim. Acta*, 1964, **47**, 1828.

[11] Singh, J., Prashar, R., Lakhanpal, M. L., and Paul, R. C., *J. Scient. Ind. Res.* B, 1962, **21**, 430.

[12] Susz, B. P., and Cassimatis, D., *Helv. Chim. Acta*, 1961, **44**, 395; Cooke, I., Susz, B. P., and Herschmann, C., *Helv. Chim. Acta*, 1954, **37**, 1280.

[13] Cook, D., *Canad. J. Chem.*, 1959, **37**, 48.

[14] Cook, D., *Canad. J. Chem.*, 1962, **40**, 445.