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THE REACTION OF METHYL PHENYL KETENE AND 1-PHENYL ETHANOL - OBSERVATION OF A NEGATIVE ENTHALPY OF ACTIVATION

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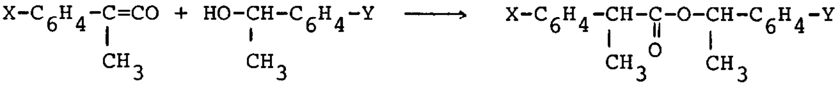
Abstract The unusual activation parameters of the reactions of aryl methyl ketenes and α-arylethanoles ($\Delta H^{\ddagger}$=-0.9 to +0.3 kcal·mol^{-1}; $\Delta S^{\ddagger}$=-68 to -71 e.u.) are interpreted by a two step mechanism via reversible formation of a small concentration of an intermediate addition complex.

For the reaction of ketenes and alcohols only scattered kinetic data are available(1-4); the reaction order varies between 2 and 4, depending on the reaction partners and conditions. In a programme designed to study asymmetric induction(5) and reaction mechanisms for one and the same reaction we became interested in the kinetics of the reaction of methyl phenyl ketene **1** (X=H) with 1-phenyl ethanol (**2**) (Y=H) in toluene.



$$X{-}C_6H_4{-}\underset{CH_3}{C}{=}CO + HO{-}\underset{CH_3}{CH}{-}C_6H_4{-}Y \longrightarrow X{-}C_6H_4{-}\underset{CH_3}{CH}{-}\underset{O}{\overset{}{C}}{-}O{-}\underset{CH_3}{CH}{-}C_6H_4{-}Y$$

1 **2** **3**

For the rate data recorded in table 1, an overall third order was deduced from the pseudo first order rate constants, k_{obs}, obtained by changing the concentration of the excess alcohol **2** used (C_0=0.24-1.3 mol/l; mole ratio **2**:**1**=11:1-65:1)(6). Quite unusual observations are: decreasing rate constants with increasing temperature(8); small and even negative activation enthalpies(9-10); extremely negative activation entropies. All this points to a mechanism involving a fast, reversible equilibrium in which a small concentration of an intermediate complex is formed. This is followed by a slow, subsequent bimolecular reaction step(11). From the steady state treatment, the following kinetics is derived(11):

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C \xrightarrow[k_2]{B} D \qquad - d[A]/dt = \frac{k_2 \cdot k_1}{k_{-1}} [A][B]^2$$

Table 1 Rates[a)] and Activation Parameters for the Reaction 1 + 2 ⟶ 3 in Toluene

1 X=	2 Y=	T (^{o}C)	$k_3 \pm \sigma$[b)] $10^3 \cdot [l^2 mol^{-2} sec^{-1}]$	z[c)]	$\Delta H^{\ddagger} \pm \sigma$[b)] $[kcal \cdot mol^{-1}]$	$\Delta S^{\ddagger} \pm \sigma$[b)] e.u.
H	H	18.7	6.7 ± 0.1	3	-0.9 ± 0.1	-71.4 ± 0.3
H	H	40.4	6.44± 0.02	7		
H	H	59.7	6.5 ± 0.18	4		
H	H	79.7	6.1 ± 0.14	4		
CH_3	H	18.8	4.6 ± 0.33	3	-0.3 ± 0.4	-70.0 ± 1.4
CH_3	H	40.4	5.3 ± 0.5	3		
CH_3	H	79.7	5.0 ± 0.6	2		
CH_3O	H	18.7	5.6 ± 0.2	2	+0.3 ± 0.2	-67.8 ± 0.6
CH_3O	H	40.4	6.5 ± 0.1	4		
CH_3O	H	59.7	7.03± 0.02	2		
CH_3O	H	79.7	7.0 ± 0.2	4		
H	Cl	21.7	2.41± 0.02	2	0 ± 0.1	-70.3 ± 0.5
H	Cl	40.4	2.97± 0.11	7		
H	Cl	59.7	2.8 ± 0.1	5		
H	Cl	79.7	2.91± 0.04	3		
H	CH_3O	40.4	14.0 ± 0.1	5		
H	H[d)]	40.4	2.06± 0.09	5		
H	H[d)]	79.7	1.9 ± 0.01	1		

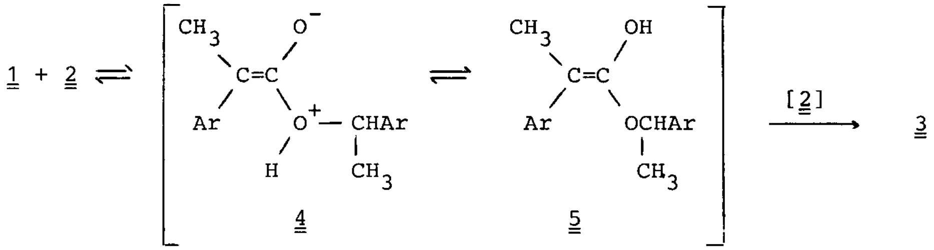
a) measured by following the decrease of absorption at 395 nm; the pseudo first order rate law was obeyed up to ≥ 95% consumption of 1;

b) σ= standard deviation; for the least square treatment see Lit.[7)]; $k_3 = k_1 \cdot k_2 / k_{-1}$;

c) z= number of kinetic runs with different concentrations of 2;

d) 1-phenylethan-D-ol.

Accordingly[11a)] $\Delta H^{\ddagger}_{exp} = \Delta H^{o}_{eq} + \Delta H^{\ddagger}_{2}$; $\Delta S^{\ddagger}_{exp} = \Delta S^{o}_{eq} + \Delta S^{\ddagger}_{2}$.
This explains the unusual values of the activation parameters in the table: each is a sum of two terms. Because ΔH^{o}_{eq} is a negative term, $\Delta H^{\ddagger}_{exp}$ can become negative also. Despite this, the overall rate remains "slow" because both entropy terms are negative, resulting in $\Delta S^{\ddagger}_{exp} \sim -70$ e.u.



We propose the following reaction sequence: a reversible addition step between alcohol and ketene, followed by ketonisation with catalysis by alcohol 2. The alternative mechanism consistently discussed in the literature[2-4)], the concerted reaction between an alcohol dimer and the ketene, seems inappropriate for several reasons. Alcohol dimers are observed only in very dilute solutions, and then only in $C \leq 5\%$, while higher aggregates are the prevalent species[12)]. The association enthalpy seems to be too small[12)] to render $\Delta H^{\ddagger}_{exp}$ negative. For a final test, the kinetics of the reaction between stoichiometric amounts of 1 (X=H) and 2 (Y=H) was measured at 19.0°C ($C_o \sim 0.4$ mol/l). If the alcohol dimer were the intermediate complex, as required by the kinetics, its concentration should not be stationary during a run and therefore third order kinetics should not be obeyed[13)]. The observation of third order kinetics for about 70% of the reaction and the reasonable agreement of k_3 ($4.2\text{-}6.9 \cdot 10^{-3}\ l^{2} \cdot mol^{-2} sec^{-1}$)[14)] with the value derived from pseudo first order kinetics therefore supports our mechanistic proposal. The mechanism is also in agreement with $k_H/k_D = 3.1\text{-}3.2$ at 40-80°C for the overall reaction (see table), and with the increase in rate when Y becomes more electron-donating (σ_p-scale) or when X becomes more electron-attracting (σ_I-scale)[15)]. Finally this mechanism leaves room for non-integral reaction orders[15)], when the substrate and reaction conditions[16)] are changed as has been observed[2-4,14)]. Qualitative observations in ether show that the rate is somewhat reduced in the more polar solvent as was observed earlier in other cases[1]. This suggests that 5 is the preferred intermediate complex instead of 4.

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8) E.Anders (Dissertation, FU Berlin 1972) has observed this phenomenon qualitatively in reactions of phenyl trifluormethyl ketene with alcohols.
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14) Because of the high sensitivity of 1 towards O_2 and other impurities a higher precision in these measurements is not within easy reach; 85-95% 3 was isolated from the kinetic runs.
15) This becomes more evident when the kinetic data for 1 (X=Cl) are taken into consideration also: $\Delta H^{\ddagger} = 0 \pm 0.7$ kcal·mol^{-1}, $\Delta S^{\ddagger} = -65 \pm 2.4$ e.u. These values were omitted from the table, because the reaction order increases between 18.8 and 79.7°C from 2.7 to 3.4.
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