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CHEMISTRY AT HIGH PRESSURES, PART II : THE ACID-INDUCED DECOMPOSITION OF DIPHENYLDIAZOMETHANE

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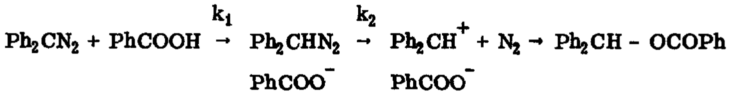
Many detailed studies have been made of the reaction between diphenyldiazomethane (DDM) and benzoic acid.[1,2,3,4] The formation of benzhydryl benzoate (IV) is believed to result from a rate-controlling proton-transfer (k_1) followed by rapid decomposition of the diazonium ion (II) k_2, and collapse of the ion-pair (III).[5]



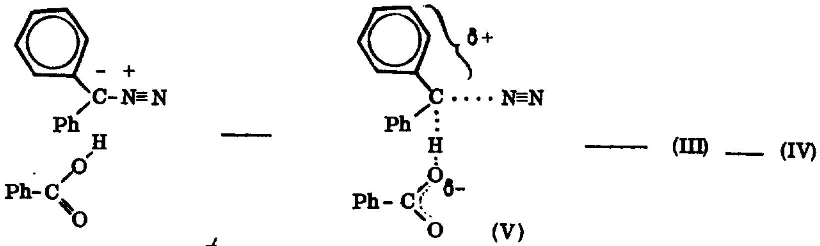
$$Ph_2CN_2 + PhCOOH \xrightarrow{k_1} \underset{PhCOO^-}{Ph_2CHN_2} \xrightarrow{k_2} \underset{PhCOO^-}{Ph_2CH^+} + N_2 \rightarrow Ph_2CH - OCOPh$$

(I) (II) (III) (IV)

The reaction of PhCOOD with I is accompanied by a substantial primary kinetic isotope effect, $k_H/k_D = 3.8$[6] and the Brønsted constant, α appears to be about 0.75.[7] These figures in conjunction with the calculations of More O'Ferrall and Kouber[8] indicate a transition state with the proton some 30% transferred to DDM.

We have now measured the pressure dependence of this reaction in dibutyl ether up to 1 kBar. The rate increases with pressure indicating a volume of activation of -13.1 cm^3 (Table).

The argument above requires substantial charge development in the transition state. Proton transfers to nitrogen have been shown to be associated with a very large value of $\Delta V^{\neq}$; for example, ammonia (water) $\Delta V^{\neq} = -29$ cm^3,[9] piperidine (MeOH) $\Delta V^{\neq} = -49.5$ cm^3.[10] These are both reactions of neutral substrates and the negative activation volume is associated with electrostriction of solvent concomitant with charge development. There is no reason to suppose that proton transfer to carbon would exhibit substantially different characteristics so that one would expect $\Delta V^{\neq} < -30$ cm^3 especially in the less polar solvent dibutyl ether.[11,12] The decomposition of the diazonium ion would be associated with a positive activation volume; values around +10 cm^3 are commonly found for unimolecular decompositions of aryldiazonium ions in water.[13] We suggest that the high value found is due to concurrent loosening of the C-N bond to pass through a transition state of the type (V).



Thus the negative contribution to $\Delta V^{\neq}$ due to ionogenesis would be compensated by a positive contribution due to bond-fission. This interpretation moreover is susceptible to further investigation as it should be accompanied by a nitrogen isotope effect. This aspect will be further investigated.

Table

P/atmos	$10^{3}k$/L mol^{-1} min^{-1}
1	41.0
200	45.5
400	50.0
600	54.5
800	57.3
1090	61.4

$$\ln k_p = -3.194 + 5.50 \times 10^{-4} P - 1.65 \times 10^{-7} P^2$$

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