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Bond energy of the IO radical from molecular beam reactive scattering measurements

THE bond energy $D_0(\text{IO})$ of the IO radical is not reliably known. An early estimate, $D_0(\text{IO}) = 44$ kcalorie mol⁻¹, was derived by Gaydon¹ from the IO emission spectrum of the CH₃I flame. Since this value was obtained by Birge-Sponer extrapolation of only five vibrational levels of the upper IO(²Π) state, it is not expected to be very accurate. The same spectrum was studied by Ramsay² in absorption by flash photolysis of O₂/I₂ mixtures. Birge-Sponer extrapolation of six bands gave $D_0(\text{IO}) = 42 \pm 5$ kcalorie mol⁻¹. But more accurate extrapolation² for ClO and BrO using twenty bands showed that extrapolation from a small number of low lying levels leads to unreliable results. A rigorous upper bound $D_0(\text{IO}) < 62.8$ kcalorie mol⁻¹ was determined from predissociation of the upper IO(²Π) state.

A value $D_0(\text{IO}) = 57 \pm 6$ kcalorie mol⁻¹ was estimated by Sugden³ by photometry of the IO emission spectrum from a O₂/H₂/I₂ (1%) flame equilibrium. Two estimates^{4,5} have been made by extrapolation of the RKR potential curve of the upper IO(²Π) state with model potentials; one⁴ supporting the higher flame equilibrium value and the other⁵ supporting the lower Birge-Sponer value.

Recently, preliminary reports⁶⁻⁸ of O atom reactive scattering by ICl have shown an important reaction path to be



In our experiments, a crossed molecular beam apparatus⁹ with an electron bombardment mass spectrometer detector was used. The O atom beam was produced from a low pressure (~1 torr) microwave discharge through O₂. The discharge region was separated from the beam source slit by ~60 cm of Pyrex tube. This configuration results in a low temperature ~350 K atom beam and suppresses O₂(¹Σ_g⁺) metastable molecules. The ICl cross beam issues from a supersonic nozzle source and has a narrow velocity distribution (~20% full

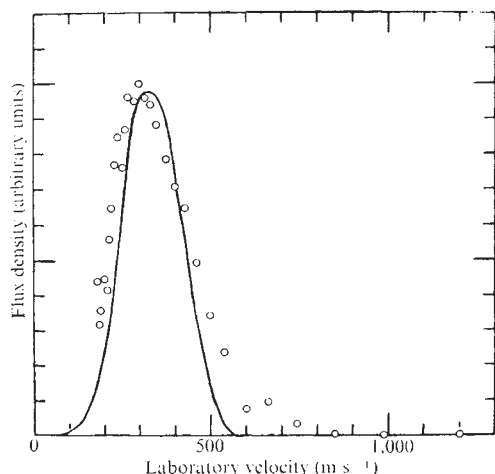


Fig. 1 Laboratory velocity distribution (flux density) of IO reaction product along the direction of the nominal centroid vector. $\text{O} + \text{ICl} \rightarrow \text{OI} + \text{Cl}$. $\Theta = 79^\circ$.

width at half maximum). The most probable reactant translational energy was $E = 0.8$ kcalorie mol⁻¹. The distributions of IO product velocities have been measured by a computer time-of-flight system over a range of laboratory scattering angles. Analysis of the full experimental data shows that the reaction proceeds by a long-lived complex mechanism.

The distribution of IO product translation energy in centre of mass coordinates is most accurately determined by observation of the IO velocity distribution along the direction of the centroid vector in laboratory coordinates. The IO flux density distribution measured at laboratory scattering angle $\Theta = 79^\circ$ (nominal centroid vector at $\Theta = 78^\circ$) is shown by open circles in Fig. 1. The distribution for the long-lived collision complex, predicted by a model¹⁰ based on RRKM theory of unimolecular decomposition, is also shown by a solid curve in Fig. 1. Agreement with the experimental data is obtained for a reaction exoergicity $\Delta D_0 = 3.4$ kcalorie mol⁻¹. Using¹¹ $D_0(\text{ICl}) = 49.6$ kcalorie mol⁻¹, we obtain $D_0(\text{IO}) = 53 \pm 3$ kcalorie mol⁻¹.

This value of $D_0(\text{IO})$ also gives good agreement with our time of flight measurement of the $\text{O} + \text{I}_2 \rightarrow \text{IO} + \text{I}$ reaction. But the exoergicity, $\Delta D_0 = 17.4$ kcalorie mol⁻¹, is greater for this reaction. Thus it does not provide as sensitive a test of $D_0(\text{IO})$ as the almost thermoneutral $\text{O} + \text{ICl}$ reaction.

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Unique form of filamentous carbon

CONSIDERABLE interest has been shown in the formation of carbon filaments from the catalytic decomposition of gases over metal surfaces at about 700° C (see refs 1, 2). Detailed studies have been chiefly confined to the behaviour of pure metals, but technically and industrially the effect of alloying elements is also important. We have studied how additives to an iron catalyst modify the filament growth process during decomposition of acetylene. With acetylene decomposed on a Pt/Fe alloy a new mode of filament growth was identified in which the complete detachment of a catalyst particle from the surface of the metal was not a necessary prerequisite for growth³. Here we describe the effect of tin on the growth of