Infrared Chemiluminescence from the Reaction of Oxygen Atoms with Simple Hydrocarbons

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ALTHOUGH discharge flow techniques involving e.s.r.[1,2] or mass spectrometric detection[3,4] can yield much kinetic data on the reactions of free atoms with hydrocarbons, their mechanisms are sometimes not uniquely determined. I.r. chemiluminescence can provide additional information because the vibrational energy distribution in a product will be characteristic of the reaction forming it. With exothermic transfer reactions the product containing the newly formed bond is normally vibrationally excited, the extent depending on the relative masses of the atoms involved and on the nature of the interactions between them.[5]

This technique can be applied to the reaction of oxygen atoms with ethylene. Brown and Thrush[1] and Niki, Daby, and Weinstock[4] favour the initial step

$$O + C_2H_4 \rightarrow CH_3\cdot + \cdot CHO + 43 \text{ kcal./mole} \qquad (1)$$

proposed by Cvetanovič[6] whereas Westenberg and de Haas[2] consider the formation of formaldehyde as a major product to be evidence for the initial step

$$O + C_2H_4 \rightarrow :CH_2 + CH_2O + 8 \text{ kcal./mole} \qquad (2)$$

suggested by Avramenko, Kolesnikova, and Savinova[7] rather than evidence for the secondary step[4]

$$O + CH_3\cdot \rightarrow H_2CO + H\cdot + 67 \text{ kcal./mole} \qquad (3)$$

These reactions can be distinguished because they involve different mechanisms for the formation of the major product, CO. For (1) + (3) it is

$$O + HCO \rightarrow OH + CO + 84 \text{ kcal./mole} \qquad (4)$$

whereas for (2) it is

$$O + CH_2 \rightarrow CO + 2H + 73 \text{ kcal./mole} \qquad (5)$$

which is an important second step in the reaction of oxygen atoms with acetylene.[1]

$$O + C_2H_2 \rightarrow CO + CH_2 + 48 \text{ kcal./mole} \qquad (6)$$

We have investigated the i.r. chemiluminescence emitted when oxygen atoms in a nitrogen carrier (produced by titrating active nitrogen with nitric oxide) react with acetylene or ethylene in a 1 litre gold-plated sphere at total pressures of 0·08—0·30 mm. Hg. In agreement with Creek and Jonathan,[8] we observe strong CO emission from levels up to $v' = 15$ (84 kcal./mole) in the $O + C_2H_2$ reaction; the dependence of the vibrational distribution on experimental conditions suggests that both (5) and (6) yield vibrationally excited CO, the former populating the higher levels, where collisional redistribution of vibrational energy causes population of levels above that corresponding to the exothermicity of reaction (5). OH Emission from the $O + C_2H_2$ reaction was extremely weak.

In contrast, we find that the $O + C_2H_4$ reaction gives strong OH emission from levels up to $v' = 3$ (29 kcal./mole) with H_2CO emission of ν_1 and of ν_4 (both 8 kcal./mole), but only weak CO emission confined to level $v' = 1$.

Thus it is clear that different mechanisms of CO production predominate in the $O + C_2H_2$ and $O + C_2H_4$ reactions, and the energies of the OH and CO emission from the latter system are those expected for reaction (4). This is excellent evidence that the mechanism of the $O + C_2H_4$ reaction is (1) + (3) + (4) and not (2) + (5). It is hoped that i.r. chemiluminescence will prove a useful tool in establishing the mechanisms of formation of particular products in the reaction of oxygen atoms with more complex hydrocarbons.

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