Heat of Formation of the t-Butoxytriphenylphosphoranyl Radical

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The heat of formation of t-butoxytriphenylphosphoranyl was measured using a photoacoustic technique and allowed the construction of a complete enthalpic profile for the formation and decay of this radical.

The structural and kinetic properties of phosphoranyl radicals have been the subject of intensive investigation.[1,2] However, no thermodynamic measurements have been made for these radicals presumably because their generally short lifetimes and high molecular weights make them inappropriate subjects for the normal gas-phase techniques.[3,4]

We have used a photoacoustic method[5] to measure the heat of formation of the t-butoxytriphenylphosphoranyl radical,[2,6] $\Delta H_f(\mathrm{Bu^tO\dot{P}Ph_3})$, in solution at 300 K. Briefly, pulses from a nitrogen laser (pulse width 10 ns; 337.1 nm; $h\nu$ 84.8 kcal mol^{-1})† were used to photolyse deoxygenated mixtures of di-t-butyl peroxide (*ca.* 0.5 M) and triphenylphosphine (*ca.* 0.04 M) in iso-octane which were flowed through a standard u.v. flow cell. The beam size was small with respect to the cell dimensions and the laser pulses gave rise to reactions (1) and (2) in the photolysis region.

$$\mathrm{Bu^tOOBu^t} \rightarrow 2\,\mathrm{Bu^tO}\cdot \quad (1)$$

$$2\,\mathrm{Bu^tO}\cdot + 2\,\mathrm{Ph_3P} \rightarrow 2\,\mathrm{Bu^tO\dot{P}Ph_3} \quad (2)$$

The heat evolved in these reactions caused a shock wave in the cell that was transmitted through the solution and was detected by a piezoelectric transducer which was clamped to

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† 1 cal = 4.18 J.

the cell wall. The signals from the transducer were stored and averaged in an oscilloscope (Tektronics 7603). Kinetic data[1,2] showed that the formation of the phosphoranyl radical was fast and that its decay, *via* reaction (3),[1] was slow when compared to the transducer response (0.5 MHz). Consequently, the system functioned as a simple calorimeter so that the measured heat of reaction, $\Delta H_{\mathrm{obs.}}$ reflected the combined thermochemistry of reactions (1) and (2) [see equation (4), where Φ is the quantum yield for peroxide photolysis].

$$\mathrm{Bu^tO\dot{P}Ph_3} \rightarrow \mathrm{Bu^t\cdot} + \mathrm{OPPh_3} \qquad (3)$$

$$\Delta H_{\mathrm{obs.}} = \Phi\,[2\Delta H_{\mathrm{f}}(\mathrm{Bu^tO\dot{P}Ph_3}) - 2\Delta H_{\mathrm{f}}(\mathrm{Ph_3P}) - \Delta H_{\mathrm{f}}(\mathrm{Bu^tOOBu^t})] \qquad (4)$$

As further confirmation, it was found that $\Delta H_{\mathrm{obs.}}$ was independent of the concentrations of $\mathrm{Bu^tOOBu^t}$ (0.20—0.75 M) and $\mathrm{Ph_3P}$ (0.02—0.15 M), after corrections have been made for light absorption by the phosphine itself which contributed to the acoustic wave.

The apparatus was calibrated using *o*-hydroxybenzophenone which is known to convert all of the light which it absorbs into thermal energy within a few nanoseconds.[7] It was found that $\Delta H_{\mathrm{obs.}} = -12.1$ kcal mol^{-1}. Taking $\Phi = 0.89$ for photolysis of di-t-butyl peroxide in iso-octane,[8] $\Delta H_{\mathrm{f}}(\mathrm{Bu^tOOBu^t}) = -81.6$ kcal mol^{-1},[9] and $\Delta H_{\mathrm{f}}(\mathrm{Ph_3P}) = 78.5$ kcal mol^{-1},[10] we obtained $\Delta H_{\mathrm{f}}(\mathrm{Bu^tO\dot{P}Ph_3}) = +30.9$ kcal mol^{-1}, equation (4).

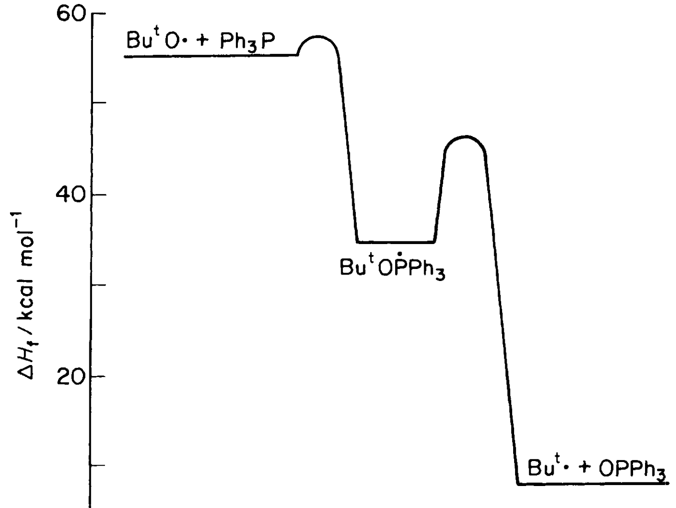

Figure 1

Combination of these thermochemical data with the activation energies[1,2‡] for reactions (2) and (3) allowed the construction of a detailed enthalpic profile§ for the formation and decay of the phosphoranyl radical, Figure 1. Clearly, while both steps are strongly exothermic, the decay of the phosphoranyl radical requires a substantial activation energy (12.1 kcal mol^{-1}).[2] The result is consistent with e.s.r. data which suggest that the radical is best described as a benzene radical anion with a phosphonium substituent, *i.e.* $\dot{\mathrm{P}}\mathrm{h}\overset{-+}{\mathrm{P}}\mathrm{Ph_2OBu^t}$.[1] Such a structure would have to undergo substantial rearrangement before fragmentation to $\mathrm{Bu^t\cdot}$ and $\mathrm{OPPh_3}$ could be achieved.

Finally, these experiments demonstrate that the photoacoustic technique can be successfully applied to thermochemical measurements which cannot be readily tackled by standard gas-phase methods.

Received, 30th May 1985; Com. 750

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‡ Reaction (2) is essentially a diffusion controlled process[2] and its activation energy was taken to be $\leqslant 3$ kcal mol^{-1} based on the temperature dependence of the solvent viscosity.

§ $\Delta H_{\mathrm{f}}(\mathrm{Ph_3PO}) = -1.2$ kcal mol^{-1}, calculated by assuming that the difference in heats of formation of triphenylphosphine and its oxide are equal to those for the methyl analogues.[10] $\Delta H_{\mathrm{f}}(\mathrm{Bu^tO\cdot}) = -21.7$ kcal mol^{-1}; L. Batt and R. T. Milne, *Int. J. Chem. Kinetics*, 1976, **8**, 59.