Relative Efficiencies of Hydrogen Abstraction by Recoil Phosphorus Atoms

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Summary The relative efficiencies of hydrogen abstraction by recoil phosphorus atoms in the gas phase were found to cover a range of two orders of magnitude for five different molecules and correlated well with a possible bond-strength effect.

THE nuclear-recoil technique has been the only successful method so far for producing phosphorus atoms and studying their chemical interactions.[1] Multivalent species may undergo abstraction, addition or even insertion reactions.[2] However, for recoil phosphorus atoms, abstraction is by far the most predominant and the only well established process.[1] Recoil phosphorus atoms in the presence of PH_3 give absolute yields of $^{32}PH_3$ as high as 78%.[1b] Phosphorus atoms also abstract fluorine atoms from PF_3 with reasonable ease.[1b,3] Nevertheless there has been no systematic study of the relative efficiencies of such abstraction reactions and no attempt to reveal the fundamental controlling factors for these abstraction reactions by multivalent species.

We have now performed systematic studies of gas-phase recoil phosphorus reactions in binary mixtures, each consisting of PF_3 and a hydrogen-containing compound, AH. The F-abstraction from PF_3 was employed here as an arbitrary standard used to compare the H-abstraction reactions for five different AH molecules. In practice, samples consisting of pure PF_3 standards and PF_3-AH mixtures were exposed to a normalized thermal neutron flux of about 1×10^{12} neutrons $cm^{-2} s^{-1}$ for 15 min. Phosphorus-32 atoms derived from the nuclear transformation, $^{31}P(n,\gamma)^{32}P$, may abstract fluorine from PF_3 or hydrogen from AH. The observed ^{32}P-labelled products, $^{32}PF_3$

and $^{32}PH_3$, were separated by the radio-gas chromatographic technique using a Porapak Q column.[4] Neither $^{32}PHF_2$ nor $^{32}PH_2F$ was observed during the analyses, but since no carrier was used for these compounds, their presence may have gone undetected.

A measurement of the H-abstraction efficiency for each AH molecule can be expressed by the specific activity ratio per bond (SARPB).

$$\mathrm{SARPB} = \left(\frac{^{32}\mathrm{PH}_3 \text{ activity per unit P-precursor}}{(\text{Mole fraction of AH}) \ (\text{No. of A–H bonds})}\right) \Big/ \left(\frac{^{32}\mathrm{PF}_3 \text{ activity per unit P-precursor}}{(\text{Mole fraction of } \mathrm{PF}_3) \times 3}\right)$$

The SARPB value was measured as a function of sample composition. For most of the molecules studied, these values were essentially nonvariant with respect to changes in composition while the other molecules had values which changed somewhat at high AH concentrations. The ideal condition for comparing the H-abstraction efficiencies of different molecules is with systems possessing similar moderation properties and therefore similar energy spectra for the reacting ^{32}P atoms. To achieve such a condition here, results from samples containing high mole fractions of PF_3 were chosen. In order to obtain reasonable counting statistics for the $^{32}PH_3$ activity, the product yields from systems containing 80% PF_3 were chosen for the SARPB calculations. The values for each of the five molecules are presented in the Table.

TABLE

Correlation between H-abstraction efficiencies and D(A–H) values

Molecule (AH)	SARPB value	D(A–H) kcal mol^{-1}	Ref for D(A–H)
CH_4	1·9 ± 0·1	104·0 ± 1	(5)
neo-C_5H_{12}	2·4 ± 0·4	99·3 ± 1	(5)
C_2H_6	5·2 ± 0·5	98·0 ± 1	(5)
SiH_4	96 ± 9	94·0 ± 2	(6)
		95·3	(7)
PH_3	162 ± 8	83·9 ± 3	(8)
		90·3	(7)

In the Table, the bond strengths in terms of the D(A–H) values are also given. The correlation between bond dissociation energy and product yield has been previously established for recoil tritium reactions where the tritium atom abstracts hydrogen from hydrocarbons,[9] but such a correlation has never before been demonstrated for any multivalent species. In the present case, it appears from the correlation that bond strength is likely to be a major factor controlling the H-abstraction process by recoil phosphorus atoms. Of course, other factors may also affect the abstraction process. The lower than expected SARPB value for neopentane may be caused by minor steric effects while the larger than expected SARPB values observed for PH_3 and SiH_4 may result from d-orbital participation in the abstraction process.

This research was supported by the U.S. Atomic Energy Commission.

(*Received*, 15*th October* 1973; *Com.* 1421.)

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