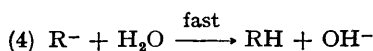
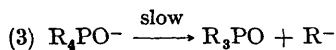
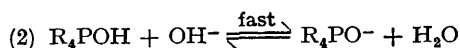
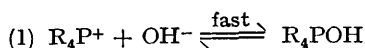


The Effect of Ferrocenyl Groups on the Decomposition of Quaternary Phosphonium Hydroxides

By ARNOLD W. SMALLEY, CHARLES E. SULLIVAN, and WILLIAM E. McEWEN
(Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01002)

THE ability of the iron-group metallocenes to stabilize an adjacent cationoid carbon atom is well known.¹ It was reported some time ago that ferrocenecarboxyaldehyde is soluble in dilute hydrochloric acid, that ferrocenylcarbinols form ethers with great ease, and that ferrocenylmethylcarbinol can be dehydrated to vinylferrocene under very mild conditions. Quantitative studies of this effect have been reported for solvolysis reactions of various ferrocenylcarbinyl acetates and for the addition of glacial acetic acid to vinylmetallocenes.

In order to determine whether or not this stabilization effect can be extended to cationic centres other than carbon, we decided to investigate the effect of ferrocenyl groups on the decomposition of quaternary phosphonium hydroxides. The mechanism for such decomposition reactions is reasonably well established and consists of the following steps:^{2,3}



If some type of stabilizing interaction between the ferrocenyl group and the cationic phosphorus atom occurs, the addition of hydroxide ion to the phosphorus atom in the first step will be inhibited. Thus, the concentration of the unstable intermediate in which phosphorus is quinquivalent will be relatively small, and, for this reason, the overall rate of decomposition of the ferrocenylphosphonium hydroxide will be relatively slow. To obtain a measure of this possible effect, we carried out the decomposition reactions of benzylferrocenyldiphenylphosphonium iodide, benzylferrocenylphenylphosphonium iodide, and benzyltriferrocenylphosphonium iodide in dimethoxyethane-water solutions of sodium hydroxide. The kinetic results are summarized in Table I.

Product ratios were also determined, the hydrocarbons by vapour-phase chromatography and the

TABLE 1

Rates of decomposition of quaternary phosphonium hydroxides in 50% dimethoxyethane-water (0.4 M in potassium chloride) at 62.2°; (R₄P⁺) = (OH⁻) = 0.012–0.020

Phosphonium Salt	k_3 (l. ² mole ⁻² min. ⁻¹)	Rel. rate
Benzyltriphenylphosphonium iodide ..	255.56 ± 5.43	1.00
Benzylferrocenyldiphenylphosphonium iodide ..	4.32 ± 0.06	1.69 × 10 ⁻²
Benzylferrocenylphenylphosphonium iodide ..	1.57 ± 0.05	6.14 × 10 ⁻³
Benzyltriferrocenylphosphonium iodide ..	0.922 ± 0.032	3.61 × 10 ⁻³

TABLE 2

Products of reactions of quaternary phosphonium iodides (1.00 g.) with 25 ml. of N-sodium hydroxide solution

Phosphonium iodide	Reflux time (hr.)	% Toluene	% Benzene
Benzyltriphenyl	8	88.3	15.1
Benzylferrocenyldiphenyl	72	95.3	3.9
Benzylferrocenylphenyl	228	58.5	1.1
Benzyltriferrocenyl	360	43.0	—

phosphine oxides by direct isolation. In one of the reactions, that of benzylferrocenylphenylphosphonium iodide with sodium hydroxide, ferrocene was also isolated in 29% yield. The results are summarized in Table 2.

It can be seen from the kinetic data that the presence of a ferrocenyl group bonded to phosphorus does indeed cause a marked depression in the rate of decomposition of a quaternary phosphonium hydroxide; thus, there is a strong interaction between the ferrocenyl group and the cationoid phosphorus atom which decreases the electrophilic reactivity of the latter. In our opinion, this interaction arises by the overlap of the nonbonding electrons of the ferrocenyl group with the 3*d*-orbitals of the phosphorus atom.

The possibility that the relatively slow rate of decomposition of a ferrocenylphosphonium hydroxide is attributable to a steric effect rather than an electronic effect can be ruled out on the basis of a theoretical argument⁴ and also on the basis of convincing experimental data involving relative rates of decomposition of benzyltris-(*p*-tolyl)phosphonium hydroxide, benzyltris-(*o*-tolyl)phosphonium hydroxide, and related compounds.⁵

Ferrocenyldiphenylphosphine, diferrocenylphenylphosphine, and triferrocenylphosphine were prepared by the methods of Sollott and co-workers,⁶ and the phosphines were converted into the iodo-benzylates in the usual manner. All new compounds synthesized gave satisfactory elemental analyses. The rate studies were conducted by potentiometric titration of unreacted sodium hydroxide with standard hydrochloric acid. All of the reactions followed the third-order rate law as required by the postulated mechanism.

In aqueous 1,2-dimethoxyethane solution containing an excess of potassium chloride the rate of reaction of benzyltriphenylphosphonium iodide with sodium hydroxide was less than that of the corresponding phosphonium chloride. However, in aqueous methanol, the iodide was found to be more reactive than the chloride. This effect is considered to be attributable to the operation of a common-ion rate depression effect in the latter medium, and this subject will be treated in greater detail in a forthcoming paper.

(Received, October 31st, 1966; Com. 841.)

¹ M. Rosenblum, "Chemistry of the Iron Group Metallocenes", Part I, ch. 2, Interscience, New York, 1965.

² W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1965, **87**, 3948.

³ W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1964, **86**, 2378.

⁴ (a) G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1962, **16**, 1426; (b) G. Aksnes and L. I. Brudvik, *ibid.*, 1963, **17**, 1616.

⁵ R. U. Pagilagan and W. E. McEwen, *Chem. Comm.*, 1966, 652.

⁶ (a) G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, 1962, **27**, 4034; (b) G. P. Sollott, H. E. Murtwoy, S. Portnoy, and J. L. Snead, *ibid.*, 1963, **28**, 1090.