PHYSICAL AND INORGANIC CHEMISTRY

Rates of Oxidation–Reduction Reactions between Ketyls and Ketones[1]

BY NOBORU HIROTA AND S. I. WEISSMAN

RECEIVED FEBRUARY 3, 1964

The kinetics for the reaction $R^-M^+ + R \rightarrow R + M^+R^-$ where M is an alkali metal and R an aromatic ketone have been determined by e.s.r. spectroscopy. The reactions are first order with respect to each of the reactants. Rate constants between 10^7 and 10^9 M^{-1} sec.$^{-1}$ and activation energies between 4 and 6 kcal. mole^{-1} were found.

Introduction

The rapid reactions between monomeric ketyls and their ketones proceed at rates which are convenient for measurement by electron spin resonance spectroscopy. Accordingly, we have investigated several such reactions in the hope of determining how solvent, structure of reactants, and possibly other factors are involved in these rates.

Results and Discussion

Preparation of the ketyls and measurements of the e.s.r. spectra were carried out by methods already described.[2,3]

All exchanges were found to be first order with respect to ketone concentration. The order with respect to ketyl was not determined in all cases. All results are consistent with first-order dependence on ketyl concentration, but in only a few cases was direct confirmation feasible.

A summary of the rate constants and apparent activation energies is given in Table I. The latter were obtained from plots of logarithm of rate constant against reciprocal of temperature. Satisfactory straight lines were found.

An argument based on the principle of detailed balance[4] requires that the transfer process is one in which the alkali metal nucleus and spin are transferred together. In several instances it has been possible to demonstrate such a mechanism directly.[5] In the limit of rapid transfer the spectrum collapses to one which exhibits only the splitting associated with the nucleus of the transferring ion. An example is shown in Fig. 1. The spectra of sodium fluorenone ketyl in DME in the absence of fluorenone and in the presence of fluorenone at 1.6 M are displayed.

In some solvents dimers of the ketyls are formed.[2] In each case the rate of reaction between the paramag-
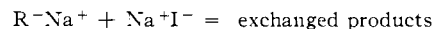
(1) This work was supported by the National Science Foundation, the United States Air Force, and the Petroleum Research Fund of the American Chemical Society to whom grateful acknowledgment is made.

(2) N. Hirota and S. I. Weissman, J. Am. Chem. Soc., 86, 2538 (1964).

(3) R. L. Ward and S. I. Weissman, ibid., 79, 2086 (1957).

(4) P. J. Zandstra and S. I. Weissman, ibid., 84, 4408 (1962).

(5) F. C. Adam and S. I. Weissman, ibid., 80, 1518 (1958).

TABLE I

RATE CONSTANTS (k) AND ACTIVATION ENERGIES (E_a) FOR TRANSFER REACTIONS BETWEEN KETYLS AND KETONES

Ketyl	Solvent	Temp., °C.	k, M^{-1} sec.$^{-1}$ $\times 10^{-8}$	E_a, kcal. mole^{-1}
		Monomers		
Na xanthone	DME	37	4.56 ± 0.25	5.1 ± 0.2
Na xanthone	THF	25	$4.48 \pm .34$	4.3 ± 0.2
Na xanthone	THP	7	$4.68 \pm .46$	
Na xanthone	Me THF	0	$4.32 \pm .18$	
Rb xanthone	DME	25	$2.50 \pm .19$	
Na benzophenone	DME	25	$1.10 \pm .04$	6.3 ± 0.2
Na benzophenone	THF	12	$1.14 \pm .10$	6
Rb benzophenone	DME	25	$1.56 \pm .22$	
K benzophenone	THF	25	~ 2.5	
		Dimers		
Mg benzophenone	DME	24	$<10^{-2}$	
Ca benzophenone	DME	24	$<10^{-2}$	
Na benzophenone	Me THF	24	$<10^{-2}$	
Na benzophenone	Dioxane	24	$<10^{-2}$	
		Free ions		
Xanthone	Aceto-nitrile	25	~ 10	

netic dimer and ketone is too slow ($k < 5 \times 10^5$ M^{-1} sec.$^{-1}$) for measurement by the e.s.r. method. In methyltetrahydrofuran, sodium benzophenone ketyl exhibits a complex superposition of spectra of monomer and dimer (Fig. 2a). Addition of 2×10^{-2} M benzophenone broadens only the lines of the monomer (Fig. 2b); addition of a large excess of benzophenone collapses the spectrum of the monomer to four lines and leaves a well resolved spectrum of the dimer (Fig. 2c). The latter resembles the spectrum of the dimer of the sodium hexamethylacetone ketyl[6] in its display of splitting by two equivalent sodium nuclei.

A process related to the oxidation–reduction reactions here discussed is the simple ion exchange

$$R^-Na^+ + Na^+I^- = \text{exchanged products}$$

In DME the reaction between sodium xanthone ketyl and sodium iodide proceeds with $k \sim 5 \times 10^8$ M^{-1} sec.$^{-1}$ at 25°. With increasing concentration of sodium

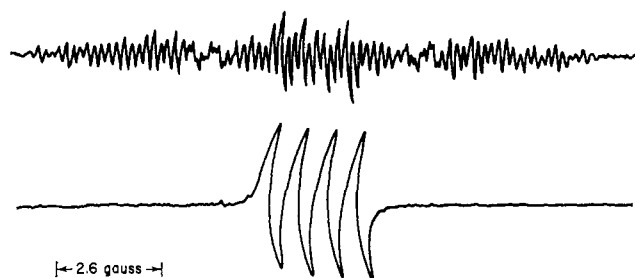(6) N. Hirota and S. I. Weissman, ibid., 82, 4424 (1960).

Fig. 1.—E.s.r. spectra of sodium fluorenone in DME: upper: spectrum of ketyl in absence of excess fluorenone; lower: spectrum after addition of fluorenone at 1.6 M.
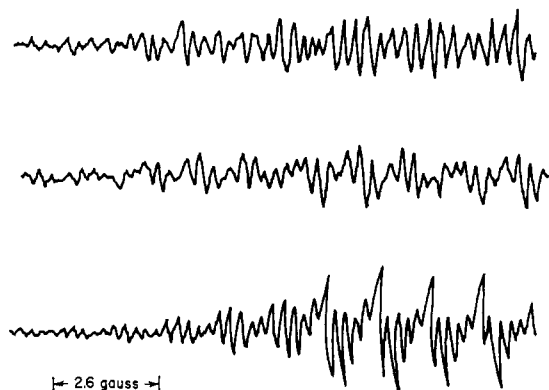

Fig. 2.—E.s.r. spectra of sodium benzophenone in Me THF: a (upper): in absence of excess benzophenone; b (middle): benzophenone added at 2×10^{-2} M; c (lower): benzophenone added at 1.5 M.
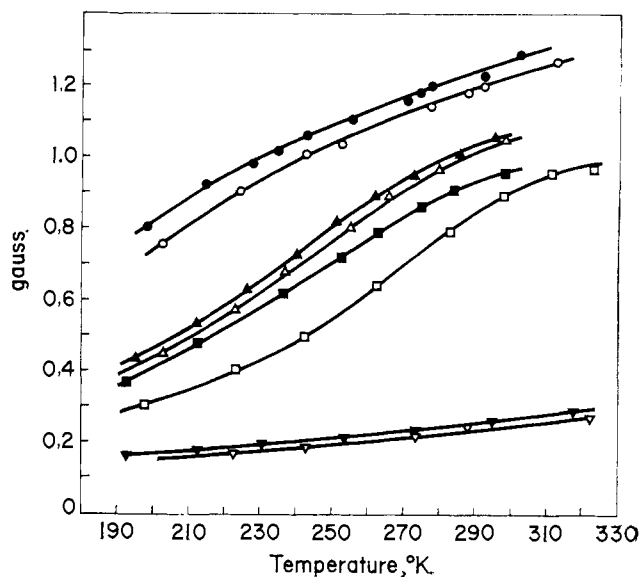

Fig. 3.—Dependence of alkali metal coupling constant on temperature: upper pair, sodium benzophenone: ●, THF; ○, DME. Central quartet, sodium xanthone: ▲, Me THF; △, tetrahydropyran; ■, THF; □, DME. Lower pair, potassium benzophenone: ▼, THF; ▽, DME.

iodide, the e.s.r. lines of the ketyl first broaden, then narrow to a spectrum which displays only proton splittings. The spectral behavior is in accord with a simple ion-exchange process.

The second-order rate constants reported above extend over more than two orders of magnitude. For a given combination of alkali metal and ketone, two parameters—solvent and temperature—determine the rate constant. Similarly, the hyperfine coupling constant with the alkali metal ion is uniquely determined by temperature and solvent. Our results suggest a

one-to-one relationship between hyperfine coupling and rate constant. Dependence of hyperfine coupling constants of the cations on temperature, solvent, and ketyl are given in Fig. 3. The four temperatures at which the sodium coupling constant in sodium xanthone is 0.9 gauss are 37, 25, 7, and 0° in dimethoxyethane, tetrahydrofuran, tetrahydropyran, and methyl tetrahydrofuran, respectively. The rate constants at these temperatures are 4.56×10^8, 4.48×10^8, and 4.32×10^8 M^{-1} sec.$^{-1}$. Although our data are not sufficient to determine whether the correlation is valid over a wider range of temperatures and solvents, they suggest that the binding of cation and anion is a determining factor in the rate. The hyperfine coupling constants of the cations are determined in part by the average conformation of the ion pair. The rates may be sufficiently sensitive to conformation to yield the correlations which we have noted.

Electronic Interaction in Ketyl Radicals[1]

By NOBORU HIROTA AND S. I. WEISSMAN

The existence of paramagnetic dimers of ketyls was confirmed from e.s.r. and optical absorption spectra. Spin–spin dipolar interactions in the dimers were studied from the e.s.r. spectra in rigid media and are discussed in connection with their structures. Slow spin exchange rates were found in the dimers. The equilibria among various forms of ketyls (paramagnetic monomer, paramagnetic dimer, and diamagnetic dimer) are discussed and several thermodynamic quantities are given for the paramagnetic monomer–dimer equilibrium. The factors which affect the equilibria are also discussed.

Introduction

The ketyls were discovered in 1891[2] and recognized as free radicals in 1911.[3] Many experiments have since

(2) F. Bechman and T. Paul, *Ann.*, **266**, 1 (1891).

been performed, not all with concordant conclusions, on the structures and chemical behavior of ketyls. We report here some of the results of our investigation of ketyls by electron spin resonance. Our experiments demonstrate that several forms of a ketyl may be in

(3) W. Schlenk and T. Weichel, *Ber.*, **44**, 1182 (1911); W. Schlenk and A. Thal, *ibid.*, **46**, 2840 (1913).