The Rates of Recombination of Cyanoalkyl Radicals in Solution

Sir:

We have had a continuing interest in the mechanism of decomposition of azo compounds.[1] The decomposition can be discussed in terms of reactions 1–4.

$$\mathrm{RN_2R} \longrightarrow \overline{2\mathrm{R}\cdot + \mathrm{N_2}} \qquad (1)$$

$$\overline{2\mathrm{R}\cdot + \mathrm{N_2}} \xrightarrow{k_c} \mathrm{RR} + \mathrm{RR'} + \mathrm{N_2} \qquad (2)$$

$$\overline{2\mathrm{R}\cdot + \mathrm{N_2}} \xrightarrow{k_d} 2\mathrm{R}\cdot + \mathrm{N_2} \qquad (3)$$

$$\overline{2\mathrm{R}\cdot} \xrightarrow{k_r} \mathrm{RR} + \mathrm{RR'} \qquad (4)$$

The products of radical recombination may be symmetrical (RR) or unsymmetrical (RR′) dimers; overlines in the equations indicate species contained in the same solvent cage. Decomposition can be effected either thermally[1] or photochemically.[2]

From the mechanism the following relationships can be derived

$$f = \frac{k_d}{k_c + k_d} = \text{fraction of radicals escaping the cage} \qquad (5)$$

$$\frac{-\mathrm{d}[\mathrm{R}\cdot]}{\mathrm{d}t} = 2k_D(1 - f)[\mathrm{R}\cdot]^2 = 2k_r[\mathrm{R}\cdot]^2 \qquad (6)$$

where k_D = the encounter rate for kinetically free radicals.

In the case of α,α'-azoisobutyronitrile (AIBN, R· = $\mathrm{Me_2\dot{C}CN}$) f has been reported to be 0.33 in benzene solution at 30°.[3] Under these conditions k_D has been calculated[4] to be $10^{10}\ M^{-1}\ \mathrm{sec}^{-1}$ so the value of k_r should be $7 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. However, measurement of k_r', the rate constant for chain termination in the radical polymerization of methacrylonitrile, by the photochemical intermittency method gives a value of $2 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$.[5]

$$2\mathrm{RCH_2CMeCN} \xrightarrow{k_r'} \text{nonradical products} \qquad (7)$$

This is surprising in view of the fact that the rate constant for chain termination is generally assumed to be independent of chain length.[6,7] The value of k_r has recently been measured using electron paramagnetic resonance to monitor concentrations of radicals formed from AIBN by thermal decomposition in naphthalene at 117 and 128°.[8] A value of $2 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ was obtained and the measured rate constants were the same at the two temperatures. The results are puzzling and may not be entirely reliable because the rates of decomposition of AIBN are expected to be rather fast under the conditions of the experiments. For this reason we decided to measure k_r for the radicals generated photochemically from AIBN and 1,1′-azocyanocyclohexane (ACC, R· = 1-cyanocyclohexyl).

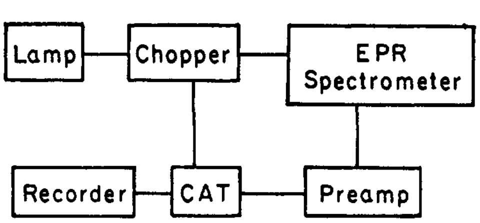


Figure 1. Experimental setup for determining rate constants.

The experimental setup is shown schematically in Figure 1. The steady-state radical concentration was determined by double integration using the strong pitch sample as a standard. The latter in turn was calibrated by double integration using carefully purified[9] diphenylpicrylhydrazyl solutions in benzene. The lamp was a 2500-W, high-pressure, mercury-xenon Hanovia lamp and the light intensity was measured by benzophenone actinometry. The rotating sector provided equal light and dark periods of approximately 2×10^{-3} sec. Each decay curve was the result of at least 10^4 scans using a computer of average transients that was triggered by the rotating sector. Samples containing 10% azo compound in benzene were degassed by several freeze–thaw cycles and irradiated in the cavity of the spectrometer. The high-resolution spectrum of the radicals produced from AIBN can be analyzed with $A_{6\mathrm{H}} = 20.3$ gauss and $A_{\mathrm{N}} = 3.3$ gauss, in excellent agreement with coupling constants reported by the earlier workers.[8]

The decay of the radical concentration during the dark periods was used to calculate the desired rate constants.

$$\frac{-\mathrm{d}[\mathrm{R}\cdot]}{\mathrm{d}t} = 2k_r[\mathrm{R}\cdot]^2 \qquad (8)$$

$$\frac{1}{[\mathrm{R}\cdot]} = \frac{1}{[\mathrm{R}\cdot]_0} + 2k_r t \qquad (9)$$

$$\Delta t = t_{1/4} - t_{3/4}$$

$$k_r = \frac{4}{3\Delta t[\mathrm{R}\cdot]_0} \qquad (10)$$

where $[\mathrm{R}\cdot]_0$ = stationary-state concentration reached during the light period.

Because of the poor signal-to-noise ratio, the data were not adequate to establish the rate law for decay, so second-order kinetics was assumed. The time required for the radical concentration to fall from three-quarters to one-quarter of the stationary-state value was measured and used to calculate k_r from eq 10.

---

(1) (a) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955); (b) O. D. Trapp and G. S. Hammond, *ibid.*, **81**, 4876 (1959); (c) G. S. Hammond, O. D. Trapp, R. T. Keys, and D. L. Nef, *ibid.*, **81**, 4878 (1959); (d) C.-H. S. Wu, G. S. Hammond, and J. M. Wright, *ibid.*, **82**, 5386 (1960); (e) G. S. Hammond, C.-H. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960); (f) G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964); (g) J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); (h) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964).

(2) P. Smith and A. Rosenberg, *ibid.*, **81**, 2037 (1959).

(3) C. Walling and V. P. Kurkov, *ibid.*, **89**, 4895 (1967).

(4) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(5) N. Grassie and E. Vance, *Trans. Faraday Soc.*, **52**, 727 (1956).

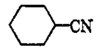
(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

(7) E. F. Caldin, "Fast Reactions in Solution," John Wiley and Sons, Inc., New York, N. Y., 1964.

(8) A. A. Bichutinskii, A. I. Prokof'ev, and V. A. Shabalkin, *Russ. J. Phys. Chem.*, **38**, 534 (1964).

(9) J. A. Weil and J. K. Anderson, *J. Chem. Soc.*, 5567 (1967).

Table I. Rate Constants for Decay of Radical Concentrations[a]

R	Theory	This study	Ref 8
Me_2CCN	7	2.2 ± 1	0.10
	7	**2.2 ± 1**	

[a] Rate constant × 10^{-9} M^{-1} sec^{-1}.

The results are not highly precise, but almost certainly accurate within the indicated limits of error, and are certainly gratifying to those who have attributed measured inefficiency in radical production to geminate recombination. The calculated diffusive encounter rate may not correspond exactly to the actual encounter rate for solute molecules[10] so the discrepancy between calculated and measured values may have no significance at all. The very large difference between the rates of recombination of small cyanoalkyl radicals and the growing radicals from methacrylonitrile is surprising and suggests that the near constancy of the reactivity of polymer radicals probably does not apply to radicals near monomeric size. There is support in the literature for such a suggestion. North and Reed have shown that the ratio of rate constants for chain termination to propagation decreases in a series of alkyl methacrylates as the alkyl group gets larger, and they have attributed this to a decrease in the termination constant.[11] Hughes and North have shown that in the low-temperature polymerization of methyl methacrylate termination reactions involving small radicals are more efficient than those involving large radicals.[12]

Further support for the high value of k_r comes from preliminary measurements at different temperatures. Stationary-state radical concentrations were measured in solutions of AIBN in *m*-xylene irradiated under identical conditions at −40 and +30°. The radical concentration changed by less than 50%, so k_r varies less than twofold between the two temperatures. A nearly diffusion-controlled rate should show very small dependence of the rate on temperature,[13] in contrast to the 5-kcal $mole^{-1}$ activation energy reported for the termination reaction of polymethacrylonitrile radicals.[5]

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479.

(10) R. M. Noyes, *J. Am. Chem. Soc.*, **86**, 4529 (1964).
(11) A. M. North and G. A. Reed, *J. Polymer Sci.*, **1A**, 1311 (1963).
(12) J. Hughes and A. M. North, *Trans. Faraday Soc.*, **60**, 960 (1964).
(13) Note that changes in solvent viscosity should have approximately, or exactly, compensating effects on the value of *f* and the diffusive encounter rate.

Steven Weiner, George S. Hammond
Contribution No. 3615, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109

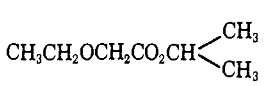
Received December 22, 1967

Rearrangement and Polar Reaction of Carbethoxymethylene in 2-Propanol

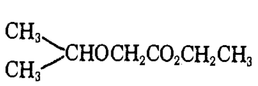
Sir:

Although intermolecular reactions of carbalkoxymethylenes are widely recorded in the literature,[1a,b] intramolecular reactions of these intermediates have not been observed.[1c] We wish to report here the rearrangement of carbethoxymethylene to ethoxyketene and its polar addition to 2-propanol as well as the *in situ* photolysis of this novel ketene.

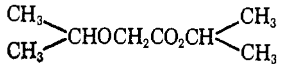
Photolysis of ethyl diazoacetate in 2-propanol solution (2 g in 150 ml) was carried out by a Hanovia (450-W) medium-pressure mercury arc with a Vycor filter. The reaction was complete in 0.5 hr when nitrogen ceased to evolve and the yellow solution became colorless. Fractionation of the reaction mixture gave little actone (2,4-DNP mp 125°) and a small amount of ethyl acetate (2–3%). Distillation of the oily residue under reduced pressure gave a volatile fraction (1.8 g, bp 80–85° (18 mm)) which was separated by preparative gas chromatography (20-ft SE-30 column) to give I–IV.



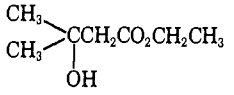
I (29%)



II (25%)



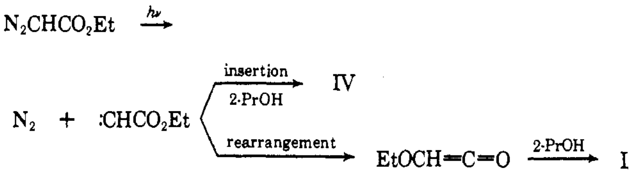
III (12%)



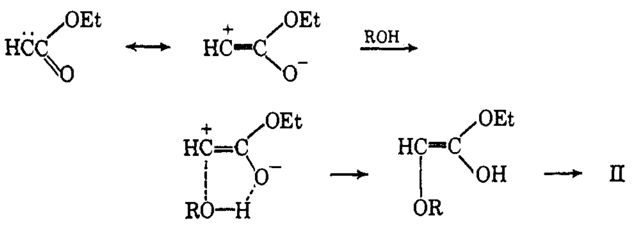
IV (9%)

All four products were structurally characterized by ir, nmr, and mass spectrometry in conjunction with unambiguous syntheses.

The products formed may be rationalized by assuming a carbethoxymethylene intermediate which inserts into the carbon–hydrogen bond to give IV. The formation of I involves a migration of the ethoxy group and most probably proceeds from an isomeric ketene analogous to the Wolff rearrangement.[2]



Product II may be explained by a polar addition of the carbene to the alcohol.



An ester interchange on II could account for III.

The possibility of the intervention of a carbonium ion produced *via* protonation of either the photoexcited

---

(1) For a review see (a) W. Kirmse "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine "Divalent Carbon," The Ronald Press, New York, N. Y., 1964. (c) Professor F. H. Westheimer has kindly called our attention to one of his earlier works (J. Shafer, P. Baranowsky, R. Laursen, F. Finn, and F. H. Westheimer, *J. Biol. Chem.*, **241**, 421 (1966)) and also an unpublished recent manuscript describing the rearrangement and insertion reactions of carbalkoxy carbenes. The observations and their interpretation are consistent with and complementary to ours.
(2) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p 38.