lengths in this molecule agree extremely closely with the corresponding distances in the head-to-head *syn* uracil photodimer[9] and the head-to-tail *anti* dimers of thymine[10] and 1-methylthymine:[11] the differences exceed 0.01 Å only in the case of the N(3)–C(2) and N(3)–C(4) bonds, where presumably the inductive effect of the methyl group in the present molecule causes a very slight lengthening of these bonds. The latter two dimers have planar cyclobutane rings; thus it appears that the conformation of the cyclobutane ring has little or no effect on the conformation of the heterocyclic rings.

The bond angles in the two halves of the dimer agree almost identically with each other. The values here also agree to within 1° with those in the head-to-tail *anti* dimers, excepting the angles at N(1) and C(5). These are smaller (~3°) than in the planar cyclobutane head-to-tail *anti* photodimers because of the puckering of the cyclobutane ring which causes C(6) to lie out of the plane of the other five thymine-nuclei atoms, and so reduces the angles at the neighboring atoms.

An outstanding feature of the structures of the thymine (and uracil) photodimers thus far elucidated is their remarkable consistency in molecular dimensions, which seems very little dependent on the nature of the pyrimidine–pyrimidine linkage (5,5:6,6 or 5,6:5,6), on the *syn* or *anti* relation of the two rings, or on the planarity of the cyclobutane ring.

The packing in the crystal is shown in Figure 4. The closest intermolecular contacts involve carbonyl oxygens and N-methyl groups and are 3.20, 3.28, and 3.30 Å. All other distances correspond to normal van der Waals contacts.

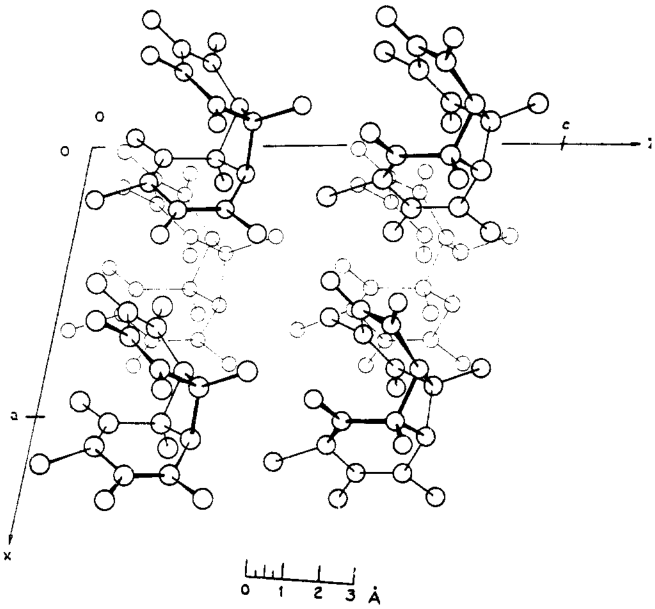


Figure 4. Intermolecular packing viewed along [010]. The bold-figured molecules at the right are related to the bold-figured ones at the left by the *c*-glide plane. The light-figured molecules are related to the bold-figured ones by translations of $a/2 + b/2$.

The ellipsoids in Figure 1 represent the relative thermal motions of the atoms, and their volumes are scaled to contain the region of 50% probability.

Acknowledgments. We thank the Medical Research Council of Canada for financial support. The phase-solving programs were written by N. C.

The Rates of Recombination of Carbon Radicals in Solution

Steven A. Weiner and George S. Hammond

Contribution No. 3687 from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California 91109.
Received June 12, 1968

Abstract: A series of azo compounds has been photolyzed in the cavity of an esr spectrometer. Use of a light-intermittency method allows estimation of the over-all rate constants (k_t) for bimolecular decay of the radicals. Comparison of the values of k_t for cumyl and a series of related radicals shows a pattern of behavior that is not easily rationalized on the basis of common structure–reactivity models. Serious discrepancies between known cage recombination parameters and the bimolecular rate constants are also noted. We tentatively suggest that relaxation of the solvent shell may play an important rate-determining role in reactions with rates close to the diffusion-controlled limit.

With the advent of electron spin resonance (esr) spectroscopy it has become possible to characterize free radicals and study the rates of their reactions by direct measurement. We have recently reported on the use of this method to measure the rate of bimolecular decay of radicals produced by photolysis of azo compounds.[1] We now wish to report the results of a more extensive study which reveals interesting reactivity relationships.

We assume that the following equations (1–6) describe the mechanism.

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

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

$$\overline{2R\cdot + N_2} \xrightarrow{k_{dis}'} R(-H) + RH + N_2 \qquad (3)$$

$$\overline{2R\cdot + N_2} \xrightarrow{k_{dc}} 2R\cdot + N_2 \qquad (4)$$

$$2R\cdot \xrightarrow{k_c} RR \qquad (5)$$

---

[1] S. A. Weiner and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 1659 (1968).

$$2R\cdot \xrightarrow{k_{\mathrm{dis}}} R(-H) + RH \qquad (6)$$

The products of the termination reactions are symmetrical dimers, RR, and disproportionation products, R(−H) and RH. In addition, unsymmetrical dimers, which may themselves be thermally and photochemically unstable, may also be formed. The esr monitoring method does not directly distinguish among the various bimolecular reactions but provides a direct measure of k_t, the sum of k_c and k_{dis}, and the rate constants for any other bimolecular processes. The termination constant for destruction of radical pairs within the solvent cage is k_t'. The following relationships can then be defined

$$a = \frac{k_t'}{k_t' + k_{\mathrm{dc}}} = \begin{array}{l}\text{fraction of radicals that}\\ \text{react within the cage}\end{array} \qquad (7)$$

$$k_t = ak_D \qquad (8)$$

$$-\frac{d[R\cdot]}{dt} = 2ak_D[R\cdot]^2 = 2k_t[R\cdot]^2 \qquad (9)$$

where k_D = the rate constant for diffusion-controlled encounter of kinetically free radicals.

If the system reaches a steady state, the following condition should hold

$$\Phi I(1 - a) = 2k_t[R\cdot]_0^2 \qquad (10)$$

where Φ = quantum yield for radical production ($2\phi_{\mathrm{RN_2R}}$), I = intensity of light absorbed by RN_2R, and $[R\cdot]_0$ = radical concentration at time t = 0 (this is the start of the dark period).

In practice the values of a for various compounds have been determined by decomposing the azo compounds in a medium which scavenges all radicals which escape for the cage.[2-5] It is clear though that such values may be obtained from eq 8 if both k_t and k_D are known. If we assume that k_D is constant for the radicals in question then relative values of k_t directly reflect the relative amounts of cage reaction.

Experimental Section

The *p,p'*-azocumenes were supplied by Professor J. Reid Shelton, azocumene itself by Professors Shelton and P. D. Bartlett, azobis-2-phenyl-3-methylbutane by Professor J. M. McBride, and azoisobutane, azoisopropane, and aozcyclohexane were synthesized by Dr. F. Haupt. Professor Bartlett also supplied azodiphenylmethane and 1-azophenylethane. The cyclohexyl radical was generated by photolysis of diphenylmercury in cyclohexane.[6] In general, good second-order plots were obtained through 70% of the decay.

Table I. Double Integration of Standard Pitch Sample

Run	Derivative peak height, cm Front cavity (F)	 Back cavity (B)	F/B[c]	DI peak height, cm	DI/F[a]	Dev[b]
1	8.0	6.8	1.2	4.8, 5.5	0.64	0.08
2	8.7	7.0	1.2	4.4, 4.4, 4.7	0.52	0.04
3	8.6	7.4	1.2	5.5, 3.8, 3.9	0.51	0.05
4	6.4	6.2	1.0	3.5, 3.5	0.55	0.01
5	7.2	6.0	1.2	3.8, 4.8, 4.8	0.62	0.06
6	8.0	6.0	1.3	5.2, 4.6, 4.5	0.60	0.04
7	6.6	5.4	1.2	3.9, 3.9	0.59	0.03
8	6.2	5.6	1.1	2.6, 3.0, 3.2	0.47	0.09
9	6.2	5.0	1.2	3.4, 3.3	0.54	0.02

[a] DI/F is the average value of the double integral divided by the derivative peak height of the front cavity. The average value of DI/F is 0.56. [b] Dev is |(DI/F) − 0.56|. The calculated standard deviation is 0.02. [c] F/B is the ratio of peak heights of standard samples in front and back cavities and should be constant for all instrument sensitivities.

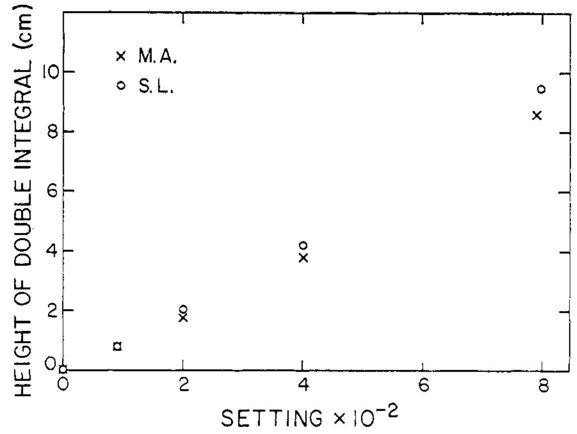


Figure 1. Peak height of double integral in centimeters as a function of instrument setting (see text).

The apparatus is essentially the same as described earlier.[1] The computer of average transients (CAT) was a Technical Measurement Corp. CAT 400, kindly loaned by Professor J. D. Roberts. The procedure used is as follows. Under conditions of steady illumination the esr spectrum was scanned to determine splitting constants. In a separate experiment on another sample, the esr spectrum was doubly integrated electronically and the peak height of the double integral (DI) was compared with that of the standard pitch sample. This sample was taken as 7.0 × 10^{-5} *M* in paramagnetic species.[1] The results of double integration of the standard pitch sample are shown in Table I. The value of the ratio of the peak height of the double integral to the derivative peak height is 0.56 ± 0.02 where 0.02 is the standard deviation. However, an examination of column 2 shows that the derivative peak height of the standard varies from day to day. To correct for this as well as differences in sensitivity caused by changing solvents, another standard pitch sample was placed in the back cavity of a dual-cavity esr spectrometer. Both derivative and double integral peak heights were then corrected for changes in instrument sensitivity. The results are listed in column 4. The front cavity uses 100-kc detection while the back cavity operates at low frequency. Because of the range of radical concentrations encountered it was necessary to show that the value of DI was linear with changes in both the modulation amplitude (MA) and the signal level (SL) settings in the 100-kc detector. The results are shown in Figure 1. For variation of SL, MA was set at 100 and *vice versa*.

For kinetic runs another sample was used. The value of $[R\cdot]_0$ was determined by comparing derivative peak heights with those of a similar sample which had been doubly integrated or with a sample of 2-cyano-2-propyl radicals or some other appropriate radical. The decay curves were obtained by setting the esr spectrometer on the largest peak in the sample and then turning on the rotating sector. The decay of radicals during the dark periods was measured using the CAT to collect data from repeated cycles. The time used for the dark period was varied from 2.2 to 5.0 msec for the radicals studied. The values of $[R\cdot]_0/[R\cdot]$ were plotted *vs.* time in accordance with eq 11, which is obtained on integration of eq 9.

$$[R\cdot]_0/[R\cdot] = 1 + 2k_t[R\cdot]_0 t \qquad (11)$$

The slope was obtained by the method of least squares. For some radicals, such as cumyl, the signal to noise ratio was too low to allow analysis using eq 11; here we used the following equation (12)

---

(2) G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, **77**, 3244 (1955).

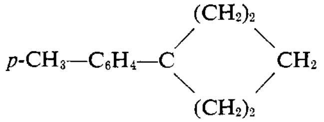
(3) (a) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 137 (1966); (b) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(4) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(5) C. Walling and V. P. Kurkov, *J. Am. Chem. Soc.*, **89**, 4895 (1967).

(6) W. A. Cramer, *J. Phys. Chem.*, **71**, 1171 (1967).

Table II. Least-Squares Analysis of Decay Curves

Radical	Solvent	No. of pts[a]	% destruction	r^b	Intercept[c]	$k[\mathrm{R}\cdot]_0 \times 10^{-3}$, sec^{-1}
$\mathrm{(CH_3)_2CCN}$	$\mathrm{C_6H_6}$	19	66–81	0.95	0.80	0.94
$\mathrm{(CH_3)_2CCN}$	$\mathrm{C_6F_6}$	20	64–70	0.92	1.12	0.48
p-$\mathrm{(CH_3)_2CHC_6H_4C(CH_3)_2}$	$\mathrm{C_6H_6}$	5	69	0.98	0.91	1.6
p-$\mathrm{BrC_6H_4C(CH_3)_2}$	$\mathrm{C_6H_6}$	6	74	0.94	0.75	1.4
$\mathrm{C_6H_5C(CH_3)CH(CH_3)_2}$	$\mathrm{C_6H_6}$	18	67–78	0.87	1.01	0.76
	$\mathrm{C_6H_6}$	12	77	0.83	1.18	0.82
$\mathrm{(CH_3)_3C}$	$\mathrm{C_6H_6}$	5	69	0.97	0.78	0.92
$\mathrm{(CH_3)_3C}$	$\mathrm{C_6H_6}$	4	64	0.95	0.82	0.84
$\mathrm{(CH_3)_3C}$	c-$\mathrm{C_6H_{12}}$	6	60	0.93	0.84	2.7

[a] In decay curve. [b] Correlation coefficient. [c] The intercept should be 1.00.

Table III. Steady-State Radical Concentrations

		$[\mathrm{R}\cdot]_0 \times 10^6$, M^{-1}	
Radical	Solvent	Double integration	Relative to $\mathrm{C_6H_6}$-$\mathrm{C(CH_3)_2}$ in $\mathrm{C_6H_6}$[a]
$\mathrm{(CH_3)_2CCN}$	$\mathrm{C_6H_6}$	0.96	1.0
	$\mathrm{C_6H_6}$	1.4	1.0
	$\mathrm{C_6H_6}$	0.83	1.0
$\mathrm{C_6H_5C(CH_3)_2}$	$\mathrm{C_6H_6}$		1.0
p-$\mathrm{CH_3C_6H_4C(CH_3)_2}$	$\mathrm{C_6H_6}$		1.3
p-$\mathrm{(CH_3)_2CHC_6H_4C(CH_3)_2}$	$\mathrm{C_6H_6}$		1.9
p-$\mathrm{BrC_6H_4C(CH_3)_2}$	$\mathrm{C_6H_6}$	3.4	3.5
$\mathrm{C_6H_5C(CH_3)CH(CH_3)_2}$	$\mathrm{C_6H_6}$	3.3	2.0
$\mathrm{CH_2(CH_2)_4CCN}$	$\mathrm{C_6H_6}$	0.75	0.73
p-$\mathrm{CH_3C_6H_4C(CH_2)_4CH_2}$	$\mathrm{C_6H_6}$	1.4	1.1
$\mathrm{(CH_3)_3C}$	$\mathrm{C_6H_6}$	1.2	1.0
$\mathrm{(CH_3)_3C}$	c-$\mathrm{C_6H_{12}}$		1.0
$\mathrm{(CH_3)_2CCN}$	$\mathrm{C_6F_6}$		1.0

[a] By comparison of derivative peak heights.

$$k_t[\mathrm{R}\cdot]_0 = 4/3\Delta t \qquad (12)$$

where Δt = the time required for $[\mathrm{R}\cdot]$ to fall from 0.75 to 0.25 of the initial value. This method tends to overestimate k_t since Δt is obtained from the steep portion of the decay curve.

Results and Discussion

In Table II we have listed the results obtained from the least-squares analysis of our decay data. In general, only four to six points were obtained from any one decay curve. The radical decay was always followed to at least 60%. Much beyond this the points were found to break off badly from the line (see Figures 2 and 3). This could well be due to the fact that the signal to noise ratio approaches one past 70% of the decay for most of the radicals in question. In Table III the values of the steady-state radical concentrations $[\mathrm{R}\cdot]_0$, as obtained by the two methods described in the Experimental Section are given. There is generally excellent agreement between the two measurements. In cases of disagreement the value obtained by double integration was used in determining k_t. It is the aforementioned agreement that leads us to believe our values of $[\mathrm{R}\cdot]_0$ are probably good to within ±20% and may even be as good as ±10%.

Table IV. Quantum Yields for Radical Production and Cage Effects in Benzene Solution at Room Temperature

R	$\Phi/2$	Ref	a	Ref
$\mathrm{(CH_3)_2CCN}$	0.47	*a*	0.67	5
$\mathrm{(CH_3)_3C}$	0.63	*b*		
$\mathrm{C_6H_5C(CH_3)_2}$	0.58	3a	0.33	3b
$\mathrm{C_6H_5C(CH_3)CH(CH_3)_2}$			<0.01	4
$\mathrm{(C_6H_5)_2CH}$			0.55	4
$\mathrm{C_6H_5CHCH_3}$			0.29[c]	*d*

[a] P. Smith and A. M. Rosenberg, *J. Am. Chem. Soc.*, **81**, 2037 (1959). [b] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966. [c] In ethylbenzene at 105°. [d] S. Seltzer and E. J. Hamilton, Jr., *J. Am. Chem. Soc.*, **88**, 3775 (1966).

The values of a and values of Φ for some azo compounds used in this study are given in Table IV. Examination of the data in Table IV shows that $1 - a$ varies from close to unity to 0.3 while Φ is roughly constant. Since the absorption characteristics of all the azo compounds are similar at long wavelength, under conditions of constant light intensity the following, relationship should exist between the steady-state radical concentrations produced from two different azo compounds.

$$\frac{k_{t,1}}{k_{t,2}} = \frac{(1 - a_1)[\mathrm{R}\cdot]_{0,2}^{2}}{(1 - a_2)[R\cdot]_{0,1}^{2}} \qquad (13)$$

This equation was used to estimate values of k_t (relative) with cumyl radical as the standard. These results, along with the absolute values of k_t, are in Table V.

Table V. Rate Constants for Decay of Radical Concentrations in Benzene Solution

Radical	k_t (abs)[a]	k_t'' (rel)[b]	k_t (rel)[c]
$\mathrm{C_6H_5C(CH_3)_2}$	8[d]	1.00	1.00
p-$\mathrm{CH_3C_6H_4C(CH_3)_2}$			0.48[e]
p-$\mathrm{(CH_3)_2CHC_6H_4C(CH_3)_2}$	1.2	0.15	0.24[e]
p-$\mathrm{BrC_6H_4C(CH_3)_2}$	0.41	0.05	0.05[e]
$\mathrm{C_6H_5CHCH_3}$			<5.00[c]
$\mathrm{C_6H_5C(CH_3)CH(CH_3)_2}$	0.23	0.03	0.06
p-$\mathrm{CH_3C_6H_4C(CH_2)_4CH_2}$	0.59	0.07	0.16[e]
$\mathrm{CH_2(CH_2)_4CCN}$	1.8[d]	0.23	0.25
$\mathrm{(CH_3)_2CCN}$	0.94	0.12	0.10
$\mathrm{(CH_3)_3C}$	0.73	0.09	0.08
$\mathrm{CH_2(CH_2)_4CH}$	0.8[f]	0.10	0.80[e]
$\mathrm{(CH_3)_2CH}$			1.2[e]
$\mathrm{(C_6H_5)_2CH}$			0.30[c]

[a] Rate constant × 10^{-9} M^{-1} sec^{-1}. [b] Ratios obtained from k_t (absolute). [c] Based on eq 13. [d] Based on eq 12. [e] Assuming $a_1 = a_2$. [f] Value taken from ref 7.

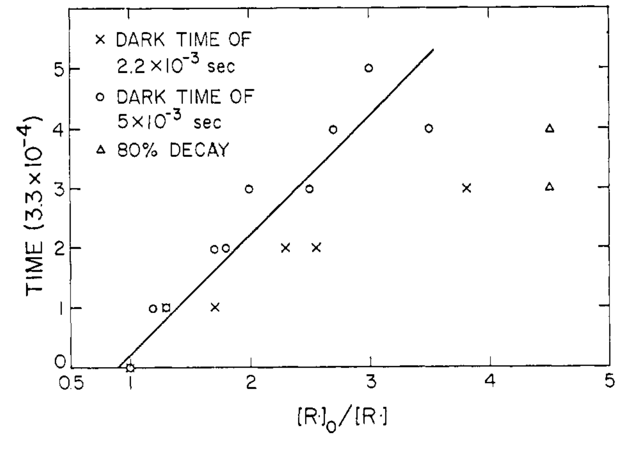


Figure 2. Decay curve for 2-cyano-2-propyl radical in benzene.

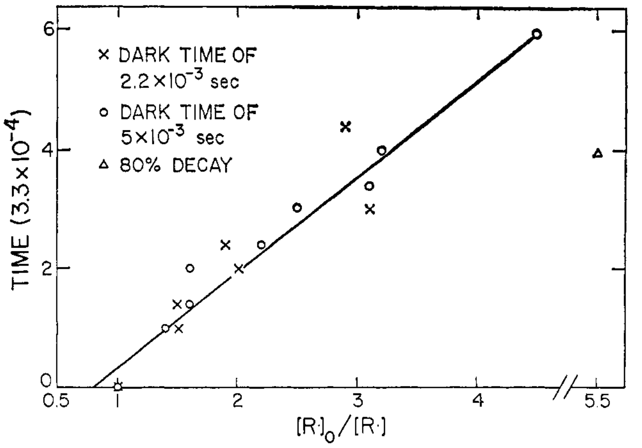


Figure 3. Decay curve for 2-phenyl-3-methyl-2-butyl radical in benzene.

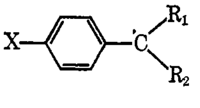
Table VI. Effect of Substituents on hfsc Values

Radical p-$XC_6H_4CR_1R_2$			hfsc				
R_1	R_2	X	R_1	R_2	H_o	H_m	X
H	H	H	16.4	16.4	5.14	1.75	6.14[a]
CH_3	CH_3	H	18	18			
CH_3	CH_3	CH_3	14	14			
CH_3	CH_3	$(CH_3)_2CH$	16	16			
CH_3	CH_3	Br	16	16	4		
CH_3	$(CH_3)_2CH$	H	16	6	5		5
H	C_6H_5	H	18				
CH_2	CH_2	CH_3	17[b]	17[b]			
2-Cyano-2-propyl			CH_3	20.3;	N	3.3	
t-Butyl			CH_3	22.5			

[a] Values obtained from A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper & Row, New York, N. Y., 1967. [b] The radical is p-$CH_3C_6H_4\underbrace{C(CH_2)_4CH_2}$.

There is fair agreement between these two methods. Unfortunately, in the cases where $[R\cdot]_0$ was too low to allow the sector to be used, the radicals were all secondary and the assumptions concerning both Φ and a are probably not very good for the comparison of secondary and tertiary radicals. This is probably responsible for the difference between relative values of k_t for the cyclohexyl radical estimated from eq 13 and calculated from the absolute value reported by Burkhart.[7] The value of 5 for k_t for the 1-phenylethyl radical must obviously be an upper limit since a for the radical at 106° is known to be 0.29[4] as compared with a value of 0.33 for the cumyl radical at room temperature.[4] Under the conditions of our experiments, a for 1-phenylethyl is undoubtedly even smaller.

The first four entries in Table V show that *para* substituents have a marked effect on the rates of bimolecular termination reactions of the cumyl radical and its derivatives. This might be due to the occurrence of variable amounts of coupling at *para* positions to form isomers of RR. However, Nelson and Bartlett[3a] showed that the parent radicals give at the most 2.2% abnormal coupling products. We anticipate that the figure should be lower for any *para*-substituted radical. Explanations based upon pure electronic effects transmitted to the benzylic position are unattractive because the difference between k_t for *p*-isopropyl and *p*-methyl is as large as any encountered.[8] Table VI shows the hyperfine splitting constants observed with the various radicals. The variations in the splitting constants (hfsc) for the hydrogen atoms of the methyl groups R_1 and R_2 of cumyl radicals and for *ortho* protons are small enough to assure us that the *para* substituents cause only small perturbations of the over-all spin distribution.



Examination of the data in Table V forces us to the interesting conclusion that *we have no respectable model to account for the variations in the rates of radical–radical reactions.* In a naive way we had anticipated that relative reactivities would be dominated by the thermodynamic stabilities of radicals with secondary effects exerting a modulating influence. The concept of relative thermodynamic stability of nonisomeric species is fuzzy at best, but most chemists schooled in chemical dynamics would probably be willing to hazard some guess as to the relative values of the heats of dissociation of a series of compounds RR to give radicals R·. These estimated values would then be taken as a measure of stabilities with respect to dimerization. Application of a postulate suggested by one of us[9] leads to two subsidiary predictions: (1) the rates of highly exothermic radical coupling reactions will vary much less than the rates of dissociation, and (2) *if all other factors are held constant the more exothermic coupling reactions will occur with the fastest rates.* Within the limits of this pseudo theory we must conclude that "other factors" are far from constant.

For example, the decay rate for cumyl radicals is 11 times as great as that of *t*-butyl radicals and the cyclohexyl radical has about the same rate as *t*-butyl. Values of k_t for *n*-pentyl ($1 \times 10^9\ M^{-1}\ sec^{-1}$) and benzyl ($4 \times 10^9\ M^{-1}\ sec^{-1}$) have been reported by Burkhart.[10,11] Steric hindrance to dimerization should be

---

[7] R. D. Burkhart, Abstracts of Papers, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 16, 1968, Paper S101.

[8] A further anomaly is encountered when di-*p*-*t*-butylazocumene is irradiated. The radical produced does not decay in the dark. Its esr spectrum consists of five lines with a 6.0-G separation between the lines. This spectrum is consistent with $R_2N\dot{N}R$ but not with $ArC(CH_3)_2$.

[9] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

[10] R. D. Burkhart, *ibid.*, **90**, 273 (1968).

[11] We are reassured as to the validity of comparison because Burkhart has reported a value ($0.8 \times 10^9\ M^{-1}\ sec^{-1}$) for the cyclohexyl radical[7] which is very close to that found by us.

about the same in cumyl and *t*-butyl leaving additional resonance stabilization of cumyl as an added stabilizing factor. Similarly, cumyl would be expected to be more "stable" than benzyl by almost any set of criteria. The fact that cumyl decays the most rapidly of the three radicals speaks clearly for the involvement of other kinetically significant factors.

Previous measurements of the relative amounts of disproportionation and symmetrical coupling products[3a,4,6,12] allow dissection of the bimolecular rate constants in contributions from coupling (k_c) and disproportionation (k_{dis}). The results are summarized in Table VII. The small variation in k_{dis} may be regarded as a reasonable corollary of the reactivity postulate,[9] but leaves us with the doubly irksome problem of accounting for the contrasting behavior of the same radical pairs in two highly exothermic processes.

Table VII. Proportioning of the Rate Constants[a] for Disproportionation and Recombination in Benzene

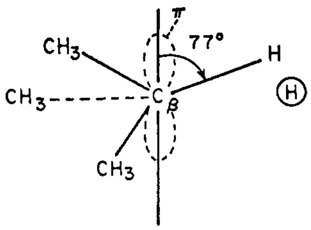
Radical	k_{dis}/k_c	Ref	k_{dis}	k_c
t-Butyl	4.6	4	6.1	1.2
2-Cyano-2-propyl[b]	0.1	*d*	0.4	4
Cumyl	0.054	3a, 11	4	76
p-Methylcumyl	0.06	12	2	32
p-Isopropylcumyl	0.1	12	1.4	11
p-Bromocumyl	0.3	12	1.0	3.0
2-Phenyl-3-methyl-2-butyl	0.3	4	0.2–0.6	0.6–1.8
Cyclohexyl[c]	1.1	6	4.2	3.8

[a] Rate constant × 10^{-8} M^{-1} sec^{-1}. [b] Assuming $k_t = 1 \times 10^9$ M^{-1} sec^{-1}. [c] The values obtained for $k_t = 0.8 \times 10^9$ M^{-1} sec^{-1}. [d] A. F. Bickel and W. A. Waters, *Rec. Trav. Chim.*, **69**, 1490 (1950).

In view of these problems we are disinclined toward rationalization of the effects of *para* substituents on the reactivity of cumyl radicals. Both *p*-methyl and *p*-bromo could conceivably "stabilize" the radicals, but this effect is already known to be of secondary significance. Furthermore, some of our unpublished studies show quite different patterns of effects of remote substituents. Similarly, we could attribute the low reactivity of the 2-phenyl-3-methyl-2-butyl compared with cumyl to simple steric hindrance in the coupling reaction. The fact that such an interpretation may ultimately prove to be correct does not camouflage the uncertainty that must now enter interpretation of all the data.

Although we are hesitant to overinterpret the reactivity data, the spin resonance spectrum of 2-phenyl-3-methyl-2-butyl radicals implies a fairly specific model for the structure of the radical.

The hfsc for protons attached to a carbon atom carrying a free electron satisfy the equation, $a_H = B\rho \cos^2 \theta$, where θ is the dihedral angle between the H–C_α–C_π and the C_α–C_π–π orbital planes and ρ is the spin density on C_π.[13] For the ethyl radical, B has a value of 58.5 G.[14] If we assume ρ for the 2-phenyl-3-methylbutyl radical is the same for C_π as for C_π in benzyl, then θ is calculated to be 77°.[15]



In the drawing the reader is viewing the model by looking along the bond connecting the isopropyl group to the benzylic carbon atom, C_π. The methyl group attached to C_π is seen to the left of the figure and aromatic ring. An examination of molecular models shows that the isopropyl group is quite restricted and that the conformation which is least hindered locates the isopropyl methyl groups above and below the plane of the benzene ring.

The work was originally undertaken with the objective of correlating values of k_t with known data for the efficiency of escape of geminate radicals from their original solvent cage. Comparisons of *a* values calculated from k_t with values measured by scavenging techniques are shown in Table VIII. Discrepancies far larger than any of the experimental inaccuracies appear. Although it is slightly reassuring to see that the slow rate of bimolecular decay of 2-phenyl-3-methyl-2-butyl correlates with an immeasurably small cage effect, we are unhappy to note that 2-cyano-2-propyl reacts so slowly that we would expect only a very small cage effect with that well-studied species.

Table VIII. Comparison of Calculated and Experimental *a* Values

	a (calcd)[a]	*a* (exptl)[b]
Cumyl	(0.33)	0.33
2-Phenyl-3-methyl-2-butyl	0.01	<0.01
2-Cyano-2-propyl	0.05	0.67
Diphenylmethyl	0.13	0.55

[a] These values are relative to cumyl radical. [b] Taken from Table IV.

One possible explanation of the inconsistency is that there is a strong interaction between the radicals and the solvent. This type of phenomenon has been previously reported.[16] Some experiments were run in cyclohexane solution and the results are shown in Table IX. It is clearly demonstrated that for the smaller radicals there is a significant solvent effect on k_t. It is interesting that Burkhart reports no such solvent effect for the cyclohexyl and benzyl radicals.[10] The slight difference in k_t for $(CH_3)_2CCN$ in benzene and hexafluorobenzene argues against a large charge-transfer interaction where the radical is the donor, while the similarity of the behavior for $(CH_3)_2CCN$ and $(CH_3)_3C$ in going from benzene to cyclohexane solvent argues against the radicals being charge-transfer acceptors. It is also reassuring to see that k_t for the *t*-butyl radical is 2.2 × 10^9 M^{-1} sec^{-1} in cyclohexane as Ingold has reported a value of 2 × 10^9 M^{-1} sec^{-1} in his solvent.[17] Our results are consistent with a stabilization of small radicals in benzene relative to cyclohexane. Evidence of a confirmatory nature is provided by the fact that for the 2-cyano-2-propyl radical the *a* value was

---

(12) J. R. Shelton, C. K. Liang, and P. Kovacic, *J. Am. Chem. Soc.*, **90**, 354 (1968).

(13) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).

(14) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(15) This calculation is not strictly valid unless C_α is either freely rotating or held rigidly in place. While neither condition is met, the calculation is included because it predicts the most stable configuration determined by playing with molecular models.

(16) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(17) D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 1055 (1968).

lower in benzene than in chlorobenzene and lower still in carbon tetrachloride.[2] Also it has been reported that for cumyl radical, a is 0.25 in benzene at 40° but is 0.35 in cyclohexane.[3a] Thus eq 7 predicts the direction of change and for cumyl radical is very close to the right order of magnitude. If we assume that carbon tetrachloride and cyclohexane are essentially nonsolvating toward the 2-cyano-2-propyl radical, eq 7 would predict a twofold increase in k_t in going from cyclohexane to benzene solution. If carbon tetrachloride interacts more strongly with the radical than cyclohexane, eq 7 predicts a greater than twofold increase in k_t.

Table IX. Effect of Solvent on Radical Termination Constants

Radical	Solvent	Method	$k_t \times 10^{-9}$ M^{-1} sec^{-1}
Cumyl	Benzene	I[a]	8
	Cyclohexane	I	8
2-Cyano-2-propyl	Benzene	I, II[b]	0.94
	Cyclohexane	I	4
	Hexafluorobenzene	I, II	0.48
t-Butyl	Benzene	II	0.73
	Cyclohexane	II	2.2
Cyclohexyl	Benzene	II	0.8[c]
	Cyclohexane	II	0.8[c]

[a] Method I involves only the comparison of derivative peak heights. [b] Method II consists of determining k_t absolutely independently in each solvent. [c] From ref 7.

If solvent effects are responsible for the poor agreement between measured and calculated a values for the cyanopropyl radical, we must assume that considerable recombination of radicals produced from azobisisobutyronitrile must occur before the radicals arrive at an equilibrium state of solvation. This hypothesis would in turn imply that the rate-limiting step in some recombination reactions may be some kind of solute–solvent relaxation process. With some trepidation we suggest that the seemingly anomalous reactivity relationships discussed above may ultimately be attributable to this effect.

Acknowledgment. We would like to thank Professors P. D. Bartlett, J. R. Shelton, and J. M. McBride, and Dr. F. Haupt for their generous gifts of the azo compounds used in this study. We also thank Professor J. D. Roberts for the use of his CAT 4000 and Mr. E. J. Hamilton for his work in design of the experimental system. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479.

The Nature of the Transition State in the Oxidation of Olefins by Chromium(VI)[1]

A. K. Awasthy and Jan Roček[2]

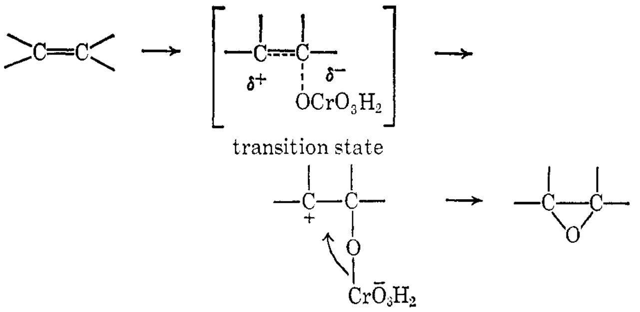
Contribution from the Department of Chemistry, University of Illinois at Chicago Circle, Chicago, Illinois 60680. *Received October 2, 1968*

Abstract: The rate of oxidation of olefins by chromic acid is determined by the total number of alkyl substituents on the double bond rather than by the degree of substitution at the most highly substituted terminus. This suggests a symmetrical structure for the transition state of the rate-limiting step of the oxidation. The relative reactivities of cyclopentene and norbornene with respect to cyclohexene are low and fall into the category characteristic for reactions with three-membered transitions states. It is therefore concluded that an epoxide is the first oxidation product and that it is formed directly from the olefin and chromium(VI).

A considerable number of studies has been devoted to the oxidation of olefins by chromic acid under a variety of conditions.[3] In a number of cases epoxides have been isolated from the oxidation and many of the products of a higher oxidation level which have been obtained could be rationalized in terms of epoxide intermediates. Nevertheless, serious arguments against the intermediacy of epoxides have been raised.[4]

Even if epoxides are intermediates in the oxidation of olefins by chromic acid, it is by no means clear whether they are formed in a reaction with chromium(VI) or whether they originate from a reaction involving either chromium(V) or chromium(IV). Further, if they are formed in the reaction of chromium(VI) and the olefin, are they formed in the rate-limiting step or as secondary products *via* an intermediate carbonium ion (Scheme I)[3,5] or cyclic chromium(IV) ester (Scheme II)?[3]

Scheme I



---

(1) This work was supported by grants of the National Science Foundation and of the U. S. Army Research Office, Durham, N. C.

(2) To whom inquiries should be directed.

(3) The subject has recently been carefully and critically reviewed. K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965.

(4) M. A. Davis and S. J. Hickinbottom, *J. Chem. Soc.*, 2205 (1958).

(5) An analogous mechanism leading to a free radical could be formulated for a one-electron oxidation. However, there is at the present time little reason to believe that a one-electron oxidation does in fact take place. Moreover, the approach used in the discussion of the carbonium ion mechanism can be applied in an analogous way to the free-radical mechanism.