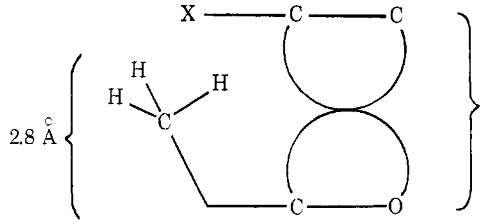
We can also view the two molecules edge-on, such that the two molecular planes are perpendicular to the paper. Consideration of bond lengths, bond angles, and atomic van der Waals radii indicates that the α-methyls extend 2.8 Å above the carbonyl plane. When X is H, ketone and quencher can approach to within 3.8–4.0 Å, very close to the van der Waals diameter of a π system. When X is methyl, with its 2-Å van der Waals radius, either R must increase or, more likely, the two molecules must tilt somewhat, decreasing k_{et} by a $\cos^2 \varphi$ factor. Of course, this description of steric effects has been applied to that mutual orientation of donor and acceptor molecules which presumably produces the greatest value of k_{et}. Energy transfer also occurs at greater R's and less favorable φ's, where steric effects would be even less significant.



The above picture must surely be tested further, but it does explain nicely the one published example of significant steric hindrance. The less efficient quenching by stilbene of a 2,6-diisopropylphenyl ketone triplet relative to the 2,6-dimethyl analog indicates a steric effect on the order of 15.[5] In this system, the large ortho substituents force the phenyl ring out of planarity with the carbonyl, ending up above and below the carbonyl, and surely prevent approach of a quencher to within van der Waals distance of the carbonyl π system.

Experimental Section

The preparations of **1** and **2** are described elsewhere.[11,12] Solvents were purified and distilled as usual.[13] Quenching studies were performed as described previously,[13] by parallel irradiation of degassed samples containing varying concentrations of quencher in a rotating turntable assembly. Relative quantum yields of cyclobutanol products at low conversion were monitored by vpc analysis. In samples containing **1** and low concentrations of either 1,3-pentadiene or 2,3-dimethyl-1,3-butadiene, irradiation resulted in decreases in the diene concentration and formation of several unidentified products not formed with other quenchers or ketones, as judged from vpc traces of the photolyzed samples. At higher diene concentrations, where most of the reaction of **1** is quenched, there was no evidence for a decrease in diene concentration.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Rate Constants for Radical Recombination. IV. The Activation Energy for Ethyl Radical Recombination[1a]

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Received December 3, 1971

Abstract: Products from the thermal decomposition of propionyl peroxide in MeI–EtI mixtures at 81° in the vapor phase have been determined. Those from radical recombination, governed by the buffer equilibrium Me· + EtI $\rightleftharpoons$ MeI + Et·, and the rate constants for radical recombination have been compared with analogous results at 142° to give an activation energy for Et· + Et· recombination of 0 ± 0.2 kcal if the absolute rate is taken as $k_{\mathrm{E}} = 10^{8.6}\ M^{-1}\ \mathrm{sec}^{-1}$. If the thermochemistry of the buffer reaction Me + EtI $\rightleftharpoons$ Et + MeI is adjusted to give k_{E} (441°K) = $10^{9.6}\ M^{-1}\ \mathrm{sec}^{-1}$, then it requires a negative activation energy for Et recombination of 2 kcal.

Previous measurements of the absolute rate for ethyl radical recombination, by sector methods,[2] or by esr spectroscopy,[3] have indicated an activation energy for the reaction of 1–2 kcal.[4] While it seems unlikely that the reaction should have an activation energy,[5] no experimental evidence has yet been adduced in favor of this supposition.

We have been encouraged to apply the method of free radical buffers[6] to this problem since the products from the sequence

$$\mathrm{Me\cdot} + \mathrm{EtI} \overset{K_{\mathrm{ME}}}{\rightleftharpoons} \mathrm{MeI} + \mathrm{Et\cdot} \tag{1}$$

$$2\mathrm{Me\cdot} \xrightarrow{k_{\mathrm{M}}} \mathrm{EtH} \tag{2}$$

$$\mathrm{Me\cdot} + \mathrm{Et\cdot} \xrightarrow{k_{\mathrm{ME}}} \mathrm{PrH} \tag{3}$$

$$\mathrm{Et\cdot} + \mathrm{Et\cdot} \xrightarrow{k_{\mathrm{E}}} \mathrm{BuH} \tag{4}$$

can be determined with fair precision. The only seri-

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[1] (a) This work has been supported, in part, by Contract No. F44620-71-C-0103 of the Air Force Office of Scientific Research and, in part, by an ACS-PRF, Type D, grant. (b) On sabbatical leave from the Department of Chemistry, Brock University, St. Catharines, Ontario, Canada.

[2] A. Shepp and K. O. Kutsche, *J. Chem. Phys.*, **26**, 1020 (1957).

[3] R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

[4] The esr determinations were carried out in liquid ethane, it is true, and may be scarcely relevant. The sector results, however, are still widely cited, and of themselves constitute sufficient motivation for this reexamination.

[5] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, **1**, 108 (1961).

[6] R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 25 (1972).

Table I. Products of Decomposition of Propionyl Peroxide[a] in EtI–MeI Mixtures at 81°

Run no.	$[Pc_2O_2]_0$[b]	$[MeI + EtI]_0$[b]	$\left[\frac{MeI}{EtI}\right]_0$	Products[c]								$\left[\frac{2BuH}{PrH}\right]\left[\frac{MeI}{EtI}\right]_{av}$
				CO_2	MeH	C_2H_4	EtH	PrH	BuH	MeI	EtI	
69	2.0	0		198	0	11.6	15.5		91.3			
70	1.2	131.8	2.09	221		10.8	20.4	31.4	68.3	7070	3910	8.48
76	3.2	129.8	2.43	169	4.6	8.6	20.5	26.0	45.4	2857	1198	8.39
77	4.0	83.0	0.627	217	1.1	12.2	20.3	13.2	89.0	787	1288	8.35
80	3.4	125.6	3.00	186	5.1	9.0	17.3	34.5	47.8	2805	933	8.31
Av				198								8.38

[a] Abbreviated as Pc_2O_2. [b] In Torr. [c] In moles, normalized to $[Pc_2O_2]_0 = 100$.

Table II. Product Balances Based on $[Pc_2O_2]_0 = 100$

Run no.	Total radicals in products[a]	ΔEtI based on products[b]	ΔEtI measd	MeH_D[c]	C_2H_{4D}[c]	$EtH_D + EtH_C$[c,d]
70	230	25.4	357	1.1	10.3	9.2 + 3.6
76	176	26.8	16	0.9	7.0	6.1 + 3.7
77	238	−6.2	13	0.8	12.5	12.0 + 0.5
80	196	35.8	1	1.2	7.6	6.4 + 6.2

[a] Equals $MeH + C_2H_4 + EtH + 2PrH + 2BuH$. This is an approximation which neglects the fraction of EtH which results from Me· + Me· and consumes two radicals. It also assumes that products from H-atom metathesis consume only one radical, whereas actually such process can consume either 0, 1, or 2 radicals.[6] The error, though small, cannot be corrected in any consistent fashion from the data in hand, and presumably accounts for the "total radicals" being fractionally in excess of the measured CO_2. [b] Ethyls generated − ethyls in RH = $CO_2 - C_2H_4 - [EtH - EtH_C] - PrH - 2BuH$. [c] The subscript D refers to products from disproportionation of radicals. Calculations are based on reported combination/disproportionation ratios for Me· and Et·.[10] [d] EtH_C = ethane from 2Me· calculated as $[PrH]^2/4[BuH]$.

ous uncertainty in comparing results at two different temperatures lies in the variation of K_{ME}, which depends on ΔG_{ME} for eq 1.

In the following, products from the introduction of ethyl radicals to mixtures of methyl and ethyl iodides at 81° are shown to be governed by eq 1–4 and are compared to earlier reported[6] analogous results at 142°.

Experimental Section

Propionyl peroxide (Pc_2O_2) was prepared by the acyl chloride–H_2O_2–pyridine method of Kochi and Mocadlo.[7] The product, bulb-to-bulb distilled under vacuum, analyzed 99+% by iodometric titration and exhibited an ir spectrum free of extraneous absorption. Other materials, reaction procedures, and analyses were as reported previously.

Results and Discussion

The Radical Source. Use of propionyl peroxide (Pc_2O_2) as a source of ethyl radicals is not without precedent.[8] However, products of the thermal decomposition of the peroxide alone in a static vapor phase system were analyzed as additional checks on the purity of the peroxide and the precision of the analytical procedure (Table I).

$$[EtCO_2\cdot]_2 \xrightarrow{\Delta} 2EtCO_2\cdot \longrightarrow 2Et\cdot + 2CO_2 \qquad (5)$$

The absolute yields of CO_2, C_2H_4, C_2H_6, and butane, based on a final pressure 3.2 times the initial, and the absence of detectable extraneous products are so close to the expected values as to be fortuitous to some degree. (The small excess of ethane over that from disproportionation of 2Et· seems typical for our particular reaction system and has been discussed elsewhere.[6–8])

The MeI–EtI System at 81°. Mixtures of the iodides, together with a small amount of Pc_2O_2, were heated at 81° for 16–20 hr, sufficient for complete decomposition of the peroxide. The products, determined by glc (Table I), are identical with those found at 142° using t-Bu_2O_2 as the radical source, excepting, of course, the absence of acetone and the presence of CO_2. The scatter in the CO_2 yields results from the difficulty in measuring an absolute value for $[Pc_2O_2]$;[9] but the average is satisfyingly near to the 200% predicted by eq 5.

Total yields of radical products are in good agreement with the CO_2 values (Table II), and the measured changes in relative MeI and EtI concentrations conform to the proportions of Me· and Et· in combination (*e.g.*, eq 1–4) and disproportionation (eq 6, 7) products.

$$Me\cdot + Et\cdot \longrightarrow MeH + C_2H_4 \qquad (6)$$

$$2Et\cdot \longrightarrow EtH + C_2H_4 \qquad (7)$$

Actually, the MeI/EtI ratio changes very little since the equilibrium (eq 1) favors Et·, and little MeI is consumed. The comparison in Table II suffers, of course, from ΔEtI being the difference in two large numbers determined to the accuracy of glc analyses, particularly for run 70.

The C_2H_4 yields agree very well with the values expected, as calculated from the PrH and BuH yields, together with Terry and Futrell's values for disproportionation *vs.* combination.[10] The excess of C_2H_4 found at 142° and thought to arise from radical attack on EtI (eq 8) is absent at the lower temperature.

$$R\cdot + CH_3CH_2I \longrightarrow RH + \cdot CH_2CH_2I \longrightarrow C_2H_4 + I\cdot \qquad (8)$$

H-Atom abstraction from all sources is also much less due partly to the lower temperature but also probably to the absence of acetone as a donor. Still the yields of MeH are a little higher than expected from disproportionation as the sole source, and EtH yields higher than the sum of disproportionation plus Me· recombination as predicted from the cross product ratio[6] (Table II).

$$[PrH]^2/4[BuH] = EtH_{combination} \qquad (9)$$

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(7) J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

(8) J. Smid and M. Szwarc, *J. Amer. Chem. Soc.*, **78**, 3322 (1956).

(9) The results for decomposition of Pc_2O_2 alone (Table I, run 69) were based on *relative* pressure changes, easier to accomplish with precision.

(10) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967).

Rate Constant and Activation Energy for Et· Recombination. Since yields of $EtH_{combination}$ are not experimentally verifiable under the circumstances, it is necessary to use the PrH and BuH yields as in the 142° work; that is,[6] from eq 1–4 and the experimentally observed value $k_{ME} = 2(k_M k_E)^{1/2}$

$$\frac{2[BuH]}{[PrH]}\left[\frac{MeI}{EtI}\right]_{av} = K_{ME}\left(\frac{k_E}{k_M}\right)^{1/2} \qquad (10)$$

The data (Table I) show the left-hand side of eq 10 to be constant over a fivefold range of MeI/EtI ratio and to equal 8.38 ± 0.05.

The equilibrium constant, K_{ME}, calculated from the same thermochemical quantities used previously[6] equals 66.6, so that $k_M/k_E = 63.6$.

To ascertain the temperature dependence of k_E, the activation energy for the measured quantity, $W = (k_E/k_M)K_{ME}^2$ can be calculated from the Arrhenius relation

$$\log \frac{W_1}{W_2} = \frac{\Delta H_W}{4.576}\frac{\Delta T}{T_1T_2} \qquad (11)$$

where W_2 at 354°K $= (8.38 \pm 0.05)^2$ and W_1[6] at 415°K $= (4.6 \pm 0.2)^2$

$$\Delta H_W = 4.576\frac{T_1T_2}{\Delta T}\log\frac{W_1}{W_2} = -5.7 \text{ kcal} \qquad (12)$$

Then, since $E_M = 0$

$$E_E = \Delta H_W - 2\Delta H_{ME(mean)} \qquad (13)$$

ΔH_{ME} at 354 and 415°K is, respectively, −2.9 and −2.8 kcal, so that $E_E = 0$.

The uncertainty in this calculation introduced from the measured quantities may be equated to twice the spread observed for $W_1^{1/2}$ and $W_2^{1/2}$ or about ±10% each. This gives rise to a joint error of ±0.6 kcal in ΔH_W.

The uncertainty introduced from ΔH_{ME} is considerably larger, of course, on the order of ±1 kcal.[6] However, the data now at hand impose narrower constraints. In our first report,[6] the value obtained for k_E, $10^{8.6}$ M^{-1} sec^{-1} (from the accepted value for $k_M = 10^{10.4}$ M^{-1} sec^{-1}), was judged too low, and an apparently more reasonable value, $10^{9.6}$ M^{-1} sec^{-1}, was shown to lie within the error limits for K_{ME} as calculated from thermochemical quantities. It now becomes evident that any such arbitrary adjustment of K_{ME} downwards (which in effect is to make ΔH_{ME} less negative) will result in a *negative* activation energy for ethyl radical recombination (eq 13). In particular, if K_{ME} is chosen so that $k_E = 10^{9.6}$ M^{-1} sec^{-1}, then $E_E = -2$ kcal. Conversely, for E_E to equal +1 or +2 kcal[2,3] requires a more negative ΔH_{ME} and an impossibly low value for k_E.

Singlet–Triplet Energy Separation, Walsh–Mulliken Diagrams, and Singlet d-Polarization Effects in Methylene

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Abstract: The singlet–triplet ($^1A_1 \leftrightarrow {}^3B_1$) energy separation in methylene has been computed by correlated *ab initio* wave functions of the highest accuracy yet reported. Results from these wave functions plus additional small corrections lead to a prediction of 11.0 ± 2 kcal/mol for the singlet–triplet energy difference. Other independent theoretical estimates also lend support to a value in this range. This relatively small separation arises primarily from the differential lowering effect produced by basis functions of d symmetry. Walsh–Mulliken (orbital energy *vs.* bond angle) diagrams are constructed and shown to be qualitatively valid representations for this molecule. Their topology is also the same for both the $^1A_1$ and $^3B_1$ states. Interpretation of these diagrams leads to a simple physical picture of the orbital distortions in the $^1A_1$ state generated by the d-polarization functions. It is demonstrated that methylene insertion and addition reactions are facilitated by d polarization. An argument as to why methylene insertion is not observed in carbon–carbon single bonds is also given.

The principal unresolved physical problem underlying carbene chemistry is the magnitude of the singlet–triplet energy separation in methylene. Because this quantity is inaccessible to direct experimental determination,[2] it has been the subject of much theoretical effort. Electronic structure theory has been notably successful in predicting a variety of properties for methylene such as geometry,[3] but the singlet–triplet

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(1) (a) Lawrence Radiation Laboratory, University of California; (b) Department of Chemistry, University of California; (c) Department of Chemistry, Princeton University.

(2) Herzberg and collaborators have carried out the most definitive study of the methylene energy level structure, and their indirect estimates led them to conclude that "...the singlet is above the triplet state, probably by less than 1 eV": G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966, pp 491, 584.

(3) On the basis of early spectroscopic studies by Herzberg [G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961); "Electronic Spectra and Electronic Structure of Polyatomic Molecules," ref 2], it was thought for some years that the triplet ground state was linear. High-accuracy theoretical calculations [J. F. Harrison and L. C. Allen, *J. Amer. Chem. Soc.*, **91**, 807 (1969); C. F. Bender and H. F. Schaefer, *ibid.*, **92**, 4987 (1970)], however, gave a bent ground state. Recent experimental evidence [E. Wasserman, W. A. Yager, and V. J. Kuck, *Chem. Phys. Lett.*, 7, 409 (1970); R. A. Berheim, H. W. Bernard, P. S. Wang, L. S. Wood, and P. S. Skell, *J. Chem. Phys.*, **53**, 1280 (1970); E. Wasserman, V. J. Kuck, R. S. Hutton and W. A. Yager, *J. Amer. Chem. Soc.*, **92**,