A New Method for Measuring the Ratios of Rate Constants for Radical Recombination[1a]

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Abstract: The rapidly established vapor phase equilibrium $R\cdot + R'I \rightleftharpoons RI + R'\cdot$ ($K_{RR'}$) provides a buffer system for radicals $R\cdot$ and $R'\cdot$ whose R–I bond energies are not far apart. In such cases it offers a powerful method for measuring ratios of rate constants for radical–radical combination. The system $Me\cdot + EtI$ has given results consistent with the equilibrium constant K_{ME} calculated from known thermochemical quantities and reported rate constants for $Me\cdot$ and $Et\cdot$ recombination, although the uncertainty in $\Delta G°$ for the equilibrium of ± 1.6 kcal translates into an error margin of $10^{\pm 0.8}$ in the recombination rate constants. By extension of the technique, it should be possible to construct a series in which the rate constant for combination of any pair of alkyl radicals is quantitatively related to that for $Me\cdot + Me\cdot$. Such a series by its requirement of internal self-consistency should permit more precise definition of both the rate constants and some of the thermochemical quantities involved.

Measurements of absolute rate constants for radical–radical combination in the gas phase are relatively few.[2] The value for $Me\cdot + Me\cdot$, $k_M \cong 10^{10.5}\ M^{-1}\ sec^{-1}$ ($E_a \cong 0$), has been obtained by several different methods[2a,3] including a direct optical observation[4,5] of $CH_3\cdot$ decrease. It is also in agreement with theoretical considerations.[3] However, for $Et\cdot + Et\cdot$[6,7] or $i\text{-}Pr\cdot + i\text{-}Pr\cdot$,[8] independent measurements do not agree even over whether such recombinations have an activation energy, let alone giving any internal consistency between k_M, k_E, and $k_{i\text{-}Pr}$. For the most part, such measurements have employed the rotating sector method[9] with its attendant difficulties.[2,8,9] In the present paper, we describe a completely independent technique for obtaining ratios of combination rate constants for pairs of radicals.

Some time ago in the course of some studies[10] on the rate of reaction of CH_3 radicals with C_2H_5I, it was found that the fastest reactions in the system were the I atom metatheses. Perusal of the rates of metathesis of halogen atoms between alkyl radicals and halogen-containing molecules[11] shows this to be a reasonable result. Cl atom transfers have activation energies of about 10 kcal/mol, similar to those for H atom metathesis. Br atom metatheses have $E \sim 6$, when corrected to a common A factor of about 10^9 l./(mol sec), so that for I atoms, the value will be about 2–4 kcal/mol. Thus in systems containing radicals and iodides, the I atom metathesis reaction will be orders of magnitude faster than any other competitive radical processes. If the system contains two organic iodides RI and R′I, having not too dissimilar C–I bond strengths, the introduction of the radicals $R\cdot$ or $R'\cdot$ will lead to a buffer system in which the ratio of concentrations (R)/(R′) is fixed by the rapid exchange

$$R'\cdot + RI \overset{K_{RR'}}{\rightleftharpoons} R'I + R\cdot \tag{1}$$

with

$$(R\cdot)/(R'\cdot) = K_{RR'}(RI)/(R'I')$$

The final products of the reaction of $CH_3 + C_2H_5I$ were found to be large quantities of ethane, propane, and butanes formed by termination reactions, *i.e.*

$$Me\cdot + EtI \overset{K_{ME}}{\rightleftharpoons} MeI + Et\cdot \tag{2}$$

$$2Me\cdot \xrightarrow{k_M} EtH \tag{3}$$

$$Me\cdot + Et\cdot \xrightarrow{k_{ME}} PrH \tag{4}$$

$$2Et\cdot \xrightarrow{k_E} BuH \tag{5}$$

The relative yields of the three hydrocarbons are governed by the equilibrium constant, K_{ME}, and the rate constants for reactions 3, 4, and 5. For simple interpretation, we require that (a) equilibrium in eq 2 is established rapidly relative to radical–radical combination, and (b) side reactions also yielding these products are small or can be accounted for by small, suitable corrections. In theory, the procedure could be extended to any pair of alkyl radicals and used to determine k_R/k_M, since K_{MR} can be calculated from thermochemical data.

$$Me\cdot + RI \overset{K_{MR}}{\rightleftharpoons} MeI + R\cdot \tag{6}$$

$$2R\cdot \xrightarrow{k_R} R\text{—}R, \text{etc.} \tag{7}$$

Viewed in reverse, to the extent that such rate constant ratios are known, the data provide a direct check on present knowledge of the thermochemical quantities.

We here report the results for the MeI–EtI system in the vapor phase with methyl radicals supplied from the

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[2] (a) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. React. Kinet.*, 1, 105 (1961); (b) S. W. Benson and H. E. O'Neal, NSRDS-NBS-21, 1970, pp 23–40.

[3] E. V. Waage and R. B. Rabinovitch, *Int. J. Chem. Kinet.*, 3, 105 (1971).

[4] H. E. Van den Berg, A. B. Callear, and R. J. Norstrom, *Chem. Phys. Lett.*, **4**, 101 (1969).

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

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

[8] E. L. Metcalfe and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4620 (1962).

[9] H. W. Melville and G. M. Burnett, *Tech. Org. Chem.*, **8**, 138 (1953).

[10] L. Batt and S. W. Benson, unpublished work, University of Southern California, 1961.

[11] A. F. Trotman-Dickenson and G. S. Milne, NSRDS-NBS-9.

Table I. Products from Decomposition of *tert*-Bu_2O_2 in the Presence of MeI and EtI at 142°

Run no.	Time, 10^3 sec	$[MeI]_0$[a]	$[MeI]_0/[EtI]_0$	Products[a] MeH	C_2H_4	EtH	PrH	BuH	AcMe	MeI	*tert*-BuOH	EtI	$(k_E/k_M)^{1/2}\cdot K_{ME}$[b]
22	85.5	467	0.36	5.65	10.07	27.37	9.92	51.10	108.8	604		1161	4.5
19	74.0	858	1.02	14.1	10.8	30.1	27.4	53.1	106.4	1056	10.2	642	4.9
8 A	3.70	815	1.07	1.06	2.83	4.99	5.14	10.85	38.4	837		736	4.7
8 B	7.32	815	1.07	0.98	4.13	8.58	10.61	21.00	74.1	856		717	4.5
7 A	8.6	734	1.15	4.05	4.37	9.30	12.55	20.90		915		455	4.9
7 B	66.2	734	1.15	10.0	8.30	24.20	28.80	43.0	162	926	10.3	444	4.4
27	68.5	1062	2.43	21.94	8.06	29.78	33.33	26.30	163.8	1188		311	4.6
9 A	3.66	860	2.78	1.07	1.45	5.02	8.71	6.04	33.2	915		254	4.2
9 B	7.26	860	2.78	1.90	2.28	8.07	15.06	10.56	58.5	925		243	4.5
												Av	4.6 ± 2
5	65[c]	852[c]	12.4[c]	0.35	0.89	16.88	19.26	3.46	97.2	855		65.2	6.2
13	7.4[d]	11.7[d]	0.0135[d]	0.27	2.84	6.59	2.35	20.69	30.5	42.3		832	0.64

[a] In arbitrary units based on $[tert\text{-}Bu_2O_2]_0 = 100$. [b] Equals $\{2(BuH)/(PrH)_H\}([MeI]_0/[EtI]_0 + \Delta[tert\text{-}Bu_2O_2][\{([MeI]_0 + [EtI]_0)/[EtI]_0^2\})$. [c] Starting at about 50% decomposition. [d] Starting at 2200 sec, no MeI present at t = 0.

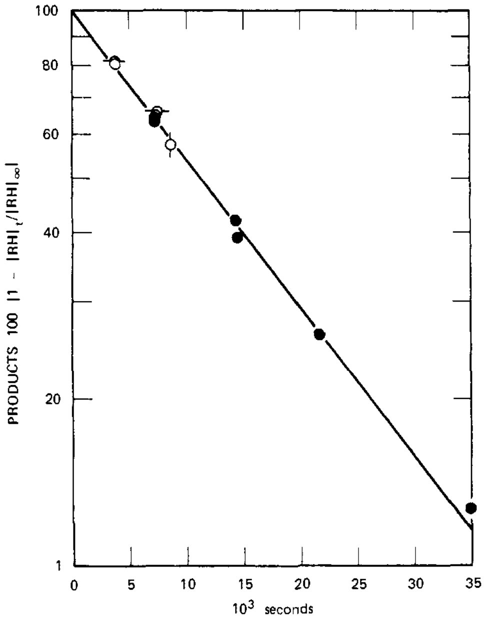

Figure 1. Yields of gaseous products *vs*. time: (●) run 29, $100\cdot[EtH]_t/[EtH]_\infty$; (ϕ) run 7; (-o-) run 8; (o) run 9; $[BuH + PrH + EtH_C + EtH_D + MeH_D + {}^1/_2MeH_H + {}^1/_2EtH_H]_t$ (Table II).

thermal decomposition of di-*tert*-butyl peroxide. Future papers will discuss *i*-Pr and *tert*-Bu radicals.

Experimental Section

Materials. Methyl iodide, ethyl iodide, and di-*tert*-butyl peroxide were supplied, respectively, by Baker, Eastman, and the Lucidol Division of Wallace and Tiernan, and were distilled prior to use. Analysis by glc showed no impurities.

Runs. A 300-cc cylindrical quartz cell thermostated at 142° was charged with reactants by conventional vacuum line techniques. The starting mixture ordinarily was comprised of 4–5 Torr of *tert*-Bu_2O_2 and 60–150 Torr of methyl plus ethyl iodides. Samples, withdrawn at intervals, were analyzed by glc, using for the most part a 6 ft × 0.25 in. Porapak Q column temperature programmed from 60 to 250°. Products were identified and quantitatively determined by comparisons with known samples. For some minor constituents additional comparisons were made on columns of molecular sieve 13X, Carbowax 20M, and silica gel for corroboration of their identities.

At first a small amount of carbon dioxide added to the initial charge was used as an internal standard. Results from these runs showed that the quantity [MeI + EtI] could be treated as constant, and, subsequently, this quantity taken as a constant served as the basis for converting peak areas into millimoles. In the absence of peroxide, neither methyl nor ethyl iodide heated for several days in the reaction cell underwent reaction

Results and Discussion

Table I and Figure 1 show results from reactions in which 4–5 Torr of *tert*-Bu_2O_2 was partly or completely pyrolyzed at 142° in the presence of a large excess of methyl and ethyl iodides. The rate of peroxide decomposition (Figure 1) was uninfluenced by the presence of the other components, the value for k_d, 5.5×10^{-5} sec^{-1}, agreeing well with the established value for unimolecular homolysis.[12] The major products (Table I), apart from acetone, are those expected from methyl and ethyl recombination. Use of CO_2 as an internal standard for some runs showed that the quantity [MeI + EtI] remained constant, within experimental error, over the course of the reaction.

Demonstration that equilibrium is established rapidly compared to recombination of radicals required that yields of the combination products be proved consistent with MeI/EtI ratios. Specifically, eq 2–5 require that yields of propane and butane be related as

$$\frac{d[BuH]}{d[PrH]} = \frac{k_E}{k_{ME}}\frac{[Et\cdot]}{[Me\cdot]} = \left(\frac{k_E}{k_{ME}}\right)K_{ME}\frac{[EtI]}{[MeI]} \qquad (8)$$

or, employing the empirically verified root mean square ratio for cross-combination[1] of Me and Et

$$\frac{d[BuH]}{d[PrH]} = \frac{1}{2}\left(\frac{k_E}{k_M}\right)^{1/2}K_{ME}\frac{[EtI]}{[MeI]} \qquad (9)$$

On integrating these relations, we find

$$\frac{k_E}{k_{ME}} = \frac{(C_4H_{10})_f(MeI)}{(C_3H_8)_f[(EtI)]K_{ME}} \qquad (10)$$

and

$$\frac{k_E}{k_M} = 4\frac{(C_4H_{10})_f^{\,2}(MeI)^2}{(C_3H_8)_f^{\,2}(EtI)^2K_{ME}^{\,2}} \qquad (11)$$

where $(C_4H_{10})_f$ is the total final concentration of C_4H_{10}, etc. For these products, whose only obvious source is radical coupling, the value $2([BuH]_f/[PrH]_f)([MeI]\cdot[EtI])_{av}$ was indeed found to be constant over a ninefold range in $([MeI]/[EtI])_{av}$[13] (Table I). Some devia-

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(12) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

(13) The "average" ratio used here is not the arithmetic mean of initial and final values, but rather the strictly accurate quantity pertaining to d[BuH]/d[PrH], *i.e.*

$$\frac{[MeI]_0}{[EtI]_0} + [(P)_0 - (P)_t]\left[\frac{1}{[EtI]_0} + \frac{[MeI]_0}{[EtI]_0^{\,2}}\right]$$

where P = *tert*-Bu_2O_2. The difference between this value and the arithmetic mean was almost negligibly small, however, in all cases.

Table II. Products[a] from Combination,[b] Disproportionation,[c] Hydrogen Abstraction,[d] and Product Balances

Run no.	22	19	8a	8b	7a	7b	27	9a	9b	13
EtH_C	0.48	3.52	0.61	1.34	1.88	4.82	10.55	3.14	5.38	0.07
EtH_D	0.89	7.17	1.46	2.83	2.82	5.80	3.56	0.81	1.42	2.79
EtH_H	20.00	19.41	2.92	4.41	4.60	13.58	15.67	1.07	1.27	3.73
MeH_D	0.36	1.00	0.18	0.38	0.45	1.03	1.20	0.31	0.54	0.08
MeH_H	5.29	13.10	0.88	0.60	3.60	8.97	20.74	0.76	1.36	0.19
$C_2H_{4total} - C_2H_{4D}$	2.81	2.70	1.18	0.92	1.10	1.47	3.3	0.32	0.31	−0.03
$\frac{[MeH_H]}{[EtH_H]}\left[\frac{[Et\cdot]}{[Me\cdot]}\right]_{av}$ [e]	4.5	3.9			3.9	3.3	3.3			
tert-Bu_2O_2 dec	99.5	99	21	36	41	98.5	98.5	21	36	31
$^1/_2$ total R· from RH products[f]	81.4	108.4	20.1	38.7	42.7	94.7	93.1	19.9	34.3	28.0
AcMe/2	54.4	53.2	19.2	37.0		81.1	81.9	16.6	29.2	15.2
Total Et in RH products[g]	146	188				141	110			
$EtI_0 - EtI_t$	137	198				192	126			

[a] In arbitrary units based on [*tert*-Bu_2O_2]$_0$ = 100. [b] $EtH_C = [PrH]^2/4[BuH]$. [c] RH_D, calculated from PrH, BuH, and k_d/k_c from ref 14. [d] RH_H, taken as remainder. [e] $[(Me\cdot]/[Et\cdot])_{av} = (1/K_{ME})([MeI]_0/[EtI]_0 + \Delta[tert\text{-}Bu_2O_2]\{([MeI]_0 + [EtI]_0)/[EtI]_0^2\})$. [f] Taken as $[BuH + PrH + EtH_C + EtH_D + MeH_D] + {}^1/_2[MeH_H + EtH_H]$. [g] Taken as $2[BuH + EtH_D] + PrH + EtH_H + MeH_D$.

tion was observed at either very large or very small MeI/EtI ratios, hardly serious in the case of run 7 (Table I). But, where the initial charge contained no MeI at all (run 13), the yield of propane, though quite small, is still much greater than predicted and suggests a minor side reaction yielding this compound (see below). In the main reaction, however, the major premises have been verified.

Side Reactions

Corollaries of eq 8 are the similar relationships for ethane and propane production.

$$\frac{d[PrH]}{d[EtH]} = \frac{k_{ME}[Et\cdot]}{k_M[Me\cdot]} = 2\left(\frac{k_E}{k_M}\right)^{1/2} K_{ME}\left[\frac{MeI}{EtI}\right] \qquad (12)$$

But the relative yields of ethane and propane (Table I) bear no simple relationship to MeI/EtI. There is too much ethane. Methane yields are also relatively large. Table II shows the amounts of both expected to arise from combination and/or disproportionation and the "excess" which presumably comes from hydrogen abstraction. For those runs in which yields were large enough to be reasonably precise after the various corrections, the ratio $[MeH/EtH]_{excess}$ is quite consistent with the [Me·/Et·] ratio for the run and yields a relative reactivity for the two radicals with respect to abstraction of 3–4. Probably C_2H_5I or acetone produced during the reaction are the major H donors (as it is when *tert*-Bu_2O_2 is decomposed alone).[12] Yields of acetone are less than quantitative, and the excess MeH and EtH yields increase relatively as the reaction proceeds (Tables I and II).

That some hydrogen abstraction from ethyl iodide occurs is indicated by the excess of ethylene over that calculated to arise *via* disproportionation[14] (Table II)

$$Me\cdot\ (Et\cdot) + EtI \longrightarrow MeH\ (EtH) + \cdot CH_2CH_2I \longrightarrow C_2H_4 + I\cdot \qquad (13)$$

Iodomethyl radicals could be produced in the system by hydrogen abstraction from MeI, and propyl and butyl radicals by addition of Me· or Et· to C_2H_4. The major fate of all such extraneous radicals would probably be to abstract iodine from MeI or EtI.

As a basis for less speculative analysis, more nearly complete product studies were carried out on *tert*-Bu_2O_2 + MeI and on *tert*-Bu_2O_2 alone, as well as on the system of interest (Table III). Of particular interest are the following: (1) the presence of *i*-PrI and *sec*-BuI, as well as *n*-PrI and *n*-BuI, in the products from MeI + EtI; (2) the production of a little EtI and methyl ethyl ketone (MEK) from the *tert*-Bu_2O_2 + MeI reaction;[15a] and (3) from the decomposition of *tert*-Bu_2O_2 alone, a small yield of propane is found, a product not found in the earlier investigation by Batt and Benson,[12,15b] since their methods of analysis precluded its

Table III. Products from Decomposition of Vapor-Phase Decomposition of *tert*-Bu_2O_2 Alone, *tert*-Bu_2O_2 + MeI, and *tert*-Bu_2O_2 + MeI + EtI at 142°

Initial composition[a]	Run no.		
	27	29–31	30
tert-Bu_2O_2	8	8	21
MeI	85	142	0
EtI	35	0	0
Products[b]			
MeH	21.9	25.8	18.6
C_2H_4	8.0	2.5	9
EtH	29.8	78.1	96.0
PrH	33.3	1.8	0.8
BuH	26.3	0.3[c]	0.2[c]
AcMe	164	174	173
MeI	1188	1775	
tert-BuOH		0.7	0.8
MEK		3.4	8.9
EtI	311	6.5	
i-BuOX[d]		Trace[c]	0.6
i-PrI	2.5	Trace[c]	
n-PrI	2.8	Trace[c]	
sec-BuI	1.5		
n-BuI	1.2		
CH_2I_2	0.6	Trace	

[a] Torr. [b] Mol/100 mol of *tert*-Bu_2O_2. For run 30, which had no internal standard, based on total products = 300, in conformity with observed pressure increase on decomposition. [c] Probable identity but not confirmed. [d] Isobutylene oxide.

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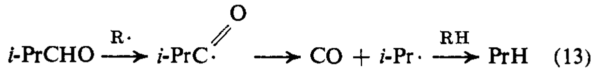
(14) J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967).

(15) (a) In the MeI + EtI system, any MEK would have been obscurred in the glc analysis by the large EtI peak. (b) Otherwise, the results agree very well, even to a comparison of MeH/EtH, which is less by a factor of 1.6. The ratio should be related to $[P_0]^{1/2}$ which gives a factor of 1.8.

identification. It *was* observed from the HCl-catalyzed decompositions where substantial yields of isobutyraldehyde offered an attractive rationale for its origin.[16]



$$i\text{-PrCHO} \xrightarrow{\text{R}\cdot} i\text{-PrC}(=\text{O})\cdot \longrightarrow \text{CO} + i\text{-Pr}\cdot \xrightarrow{\text{RH}} \text{PrH} \quad (13)$$

Taken together, these results strongly suggest not only that some hydrogen abstraction from the termination products EtH, PrH, and BuH takes place but also that the resulting radicals undergo some coupling as well as abstracting iodine from the main constituents.

The reasonableness of these premises can be readily tested using known rate constants. For example, the yield of EtI from the decomposition of *tert*-Bu_2O_2 in MeI can be explained by abstraction from EtH, followed by the reaction of Et· with MeI. That is

$$\frac{\mathrm{d[EtI]}}{\mathrm{d}t} \cong \frac{\mathrm{d[Et\cdot]}}{\mathrm{d}t} = k_{\mathrm{H}}[\mathrm{Me\cdot}][\mathrm{EtH}] \quad (14)$$

$$(\mathrm{Me}) = \left(\frac{k_{\mathrm{d}}}{k_{\mathrm{M}}}\right)^{1/2}[\mathrm{P}]^{1/2} = \left(\frac{k_{\mathrm{d}}}{k_{\mathrm{M}}}\right)^{1/2}[\mathrm{P}]_0^{1/2}e^{-k_{\mathrm{d}}t/2} \quad (15)$$

where P = peroxide and k_d its rate constant for homolysis.

$$(\mathrm{EtH}) \cong [\mathrm{P}]_0[1 - e^{-k_{\mathrm{d}}t}] \quad (16)$$

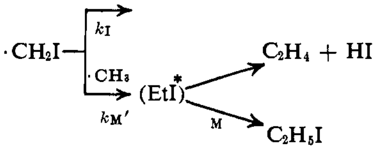
since EtH is the main product of peroxide. Substituting and integrating over 0 to t

$$[\mathrm{EtI}]_t = k_{\mathrm{H}}\left(\frac{k_{\mathrm{d}}}{k_{\mathrm{M}}}\right)^{1/2}[\mathrm{P}]_0^{3/2}\frac{2}{k_{\mathrm{d}}} \times$$
$$[(1 - e^{-k_{\mathrm{d}}t/2}) - \frac{1}{3}(1 - e^{-3k_{\mathrm{d}}t/2)})] \quad (17)$$

Taking $[\mathrm{EtI}]_t$ and $[\mathrm{P}]_0$ from Table III, $k_M = 10^{10.5}$ and $k_d = 10^{-4.2}$ gives a value for k_H of $10^{3.15}$. Published values[11] for k_H average $10^{2.9}$ at 142°, different from the derived value by a factor of 1.7.

Comparison of yields of propyl and butyl iodides in the MeI + EtI system with the yields of PrH and BuH (Table III) readily shows that a similar exercise would yield an equally reasonable result. Although in this run the concentration of Me· is lower, about $^1/_5$ that of Et·, its rate constant for abstraction from PrH or BuH is higher ($10^{3.5-3.9}$), and k_H for Et· + BuH is on the order of $10^{2.5}$.[11]

Radical combination as the source of the EtI can also be rationalized, though less precisely, using the yield of CH_2I_2 as a point of comparison.



(18)

Letting $k_{M'} \cong k_M$ and taking a reasonable value for $k_I = 10^{8.5-9/\theta 17}$

$$\left[\frac{(\mathrm{EtI})}{(\mathrm{CH_2I_2})}\right]_t = \frac{10^{10.5}}{10^{3.75}}\frac{1}{[\mathrm{MeI}]_0}\int_0^t[\mathrm{Me\cdot}] = 0.56 \quad (19)$$

While the yield of CH_2I_2 was difficult to determine accurately, its presence in a measurable amount infers a similar amount of EtI by this route.

Product Balances

The major accounting for methyls and ethyls is unambiguous. PrH and BuH are measured, and the ethane from combination, MeH, EtH, and C_2H_4 from disproportionation can be computed from those values (Table II). The contribution from "excess" MeH (or EtH) is less easy to evaluate since each MeH could account for 0, 1, or 2 methyl radicals, *viz.*

$$(0) \quad \mathrm{Me\cdot} + \mathrm{XH} \longrightarrow \mathrm{MeH} + \mathrm{X\cdot} \xrightarrow{\mathrm{MeI}} \mathrm{Me\cdot} + \mathrm{XI}$$

$$(1) \quad \mathrm{Me\cdot} + \mathrm{XH} \longrightarrow \mathrm{MeH} + \mathrm{X\cdot}$$
$$2\mathrm{X\cdot} \longrightarrow \mathrm{X{-}X}$$

$$(2) \quad \mathrm{Me\cdot} + \mathrm{EtI} \longrightarrow \mathrm{MeH} + \mathrm{C_2H_4} + \mathrm{I\cdot}$$
$$\mathrm{I\cdot} + \mathrm{Me\cdot} \longrightarrow \mathrm{MeI}$$

Each of these routes contributes, although the data do not permit an accurate assessment of the relative proportions. It seemed reasonable to let each "excess" MeH to account for, on the average, one Me· and, likewise, one Et· for each "excess" EtH. This expedient had the virtue of providing very good product balances (Table II).

The assumption also permits comparison of expected with actual conversions of EtI to MeI during the course of reaction (Table II). The experimental value suffers from being the difference of two large numbers, each determined by glc and accurate to perhaps ±2%. The error limits for $[\mathrm{EtI}]_0 - [\mathrm{EtI}]_t$ are thus ±10–20%, comparable to the observed standard deviation for the value calculated from the other products.

Comparison of Thermodynamic and Kinetic Results

Table IV shows the calculation of K_{ME} at 142° from the best current thermodynamic parameters. This value of 38 compares to a value of 6.5 determined from the propane/butane yields[18] (Table I), assuming that

Table IV. Thermodynamic Parameters[a] for Calculation of K_{ME}[b,c]

	MeI	EtI	Me·	Et·
$\Delta H_{f,298}$	3.3	−2.1	34.0	26.0 ± 1
$S°_{298}$	60.5	71.5	46.4	58.3
$C_{p,300}$	10.6	15.8	9.2	11.1
$C_{p,500}$	14.0	22.4	10.8	16.3

$\Delta G_{298} = -2.6 - T[0.9] = -2.9$
$\Delta C_{p,300} = -3.3$
$\Delta C_{p,500} = -2.9;\ \langle \Delta C_p \rangle = -3.1$
$\Delta H_{415} = -2.6 - 3.1\ (117) = -3.0$
$\Delta S_{415} = 0.9 - 3.1 \ln 415/298 = -0.1;\ T\Delta S = -0.04$
$\Delta G_{415} = -3.0$
$\mathrm{Log}\ K_{415} = 1.60;\ K = 38$

[a] Units are kcal/mol for ΔH and ΔG; gibbs/mol for C_p and S. C_p and $S°$ (Me) are from JANAF. [b] S. W. Benson and D. M. Golden, *Chem. Rev.*, **69**, 125 (1969). [c] S. W. Benson and H. E. O'Neal, *Int. J. Chem. Kinet.*, **1**, 221 (1969).

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(16) M. Flowers, L. Batt, and S. W. Benson, *J. Chem. Phys.*, 37, 2662 (1962).

(17) This reaction is endothermic by 5 kcal.

(18) It will be noted that the kinetic result rests directly on the yields of propane. Any contribution to the total amount from sources other than Me· + Et· would give values of K_{ME} (kinetic) lower than the true value. While the experiments where *tert*-Bu_2O_2 was decomposed alone or in the presence of only MeI or EtI suggest that there may be an extraneous source of propane, the amounts are, on the average, less than

$k_E = 10^{10.2}$ l./(mol sec), as reported.[6,19] To bring the values into agreement unilaterally would require that either ΔG°_{415} be in error by 1.4 kcal or that k_E be only $10^{8.7}$ l./(mol sec). This latter is improbably low but may be taken as a lower limit for the recombination of ethyl radicals. It suggests that the main source of disagreement is cumulative errors in the thermodynamic parameters.

The uncertainty in ΔG°_{415} is about ±1.6 kcal, which is well within the above limits and shows very good agreement between calculated and observed values. The chief contribution to these uncertainties in ΔG° are the heats of formation of the two radicals. The ΔH°_f and S° values for MeI and EtI are much better known and have between them a combined uncertainty which amounts to less than 0.5 kcal contribution to ΔG°.

Fessenden's reported values[7] for k_E obtained by direct esp measurement of Et· disappearance, albeit in liquid ethane, extrapolate to $10^{9.7}$ l./(mol sec) at 415°K. This yields a K_{ME} (kinetic) of 12, in substantially better agreement with the thermodynamic calculation.

Both Shepp and Kutschke[6] and Fessenden[7] report activation energies for Et· + Et· of 2.0 and 0.8 kcal/mol, respectively. While the present data have no bearing on this aspect, the desirability of further measurements at lower temperatures is indicated.

10% of the propane yields from which K_{ME} (kinetic) was determined. Furthermore, any such adjustments of this sort should also attempt to take into account propane and butane consumed during the course of reaction. That the effects of such side reactions are small and perhaps even self-compensating is evident from the invariance of K_{ME} (kinetic) with extent of reactions (Table I).

(19) Taking the average of the values at 50 and 100° in ref 6 and assuming that the recombination has no activation energy.

Steric Effects on Phosphorus Hyperfine Coupling Constants in Nitroaromatic Anion Radicals[1]

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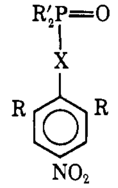
Abstract: Electron spin resonance spectra of the anion radicals produced by electrolytic reduction of 4-nitrophenyl diphenylphosphinate (I), 2,6-dimethyl-4-nitrophenyl diphenylphosphinate (II), 2,6-diphenyl-4-nitrophenyl diphenylphosphinate (III), *O,O*-diphenyl *S*-4-nitrophenyl thiophosphate (IV), and diethyl 2,6-dimethyl-4-nitrobenzylphosphonate (V) have been observed. The magnitude of the phosphorus hyperfine coupling constant, a_P, varied from 6.07 G for the anion radical obtained from I in acetonitrile to 27.15 G for the anion radical of IV in dimethylformamide. In the series of similar radicals I–III, a_P increases with increased bulk of the substituents in the 2 and 6 positions on the nitroaromatic ring. These data, in addition to comparison of data for V with data reported previously for its unmethylated analog, support the suggestion made previously that the magnitude of a_P contains an angular dependence similar to that found for proton hyperfine couplings when spin transmission occurs *via* hyperconjugation.

Stereochemical effects upon ^{31}P hyperfine coupling constants in nitroaromatic anion radicals have been of interest to us for some time. In a previous report[2] we described the electron spin resonance (esr) spectra of seven such radicals obtained by one electron reduction of phosphates and a phosphonate. We report now the extension of that work to a new series of nitroaromatic phosphorus anions derived from compounds I–V.

Our previous results[2] suggested that steric perturbations of the bonds linking the phosphorus atom to the nitroaromatic moiety (P–X–C) are important in determining the magnitude of the ^{31}P hyperfine interaction. The results reported now substantiate and elaborate this suggestion and provide sufficient data to permit some semiquantitative estimates of the parameters which describe a_P.



I, R = H; R' = C_6H_5; X = O
II, R = CH_3; R' = C_6H_5; X = O
III, R = C_6H_5; R' = C_6H_5; X = O
IV, R = H; R' = C_6H_5O; X = S
V, R = CH_3; R' = C_2H_5O; X = CH_2

Experimental Section

Solvents for electrochemistry and tetraethylammonium perchlorate supporting electrolyte were commercially available and purified according to established literature procedures. Diphenyl chlorophosphate, diphenylphosphinic acid, triethyl phosphite, and 4-nitrothiophenol were obtained from Aldrich Chemical Co. Mucobromic acid, 1,3-diphenyl-2-propanone, triethylamine, and thionyl chloride were supplied by Eastman Organic Chemicals and 3-pentanone came from Matheson Coleman and Bell. 2,6-Dimethylbenzoic acid was obtained from K & K Laboratories.

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969. Address correspondence to the Department of Chemistry, Florida State University, Tallahassee, Fla.

[2] W. M. Gulick, Jr., and D. H. Geske, *J. Amer. Chem. Soc.*, **88**, 2928 (1966).