determining step cannot be defined. Any theoretical model for a single transition state[15] for such reactions will give unrealistic results unless proper account is taken of the composite nature of the over-all process. The present model is proposed as a way of adjusting for this situation. Another valuable property of the intercepts is their temperature dependence. If rates of oxygen atom scrambling and destruction of acetyl peroxide as well as yield data for methyl acetate were available at several temperatures, and several viscosities, then $\Delta\Delta E_a$ for k_2/k_{-1} could be obtained. The $(\Delta\Delta E_a)$ would then reflect the difference in activation energies for the two combination (k_{-1}) processes since decarboxylation (k_2) of the same species is involved in each case.

The main purpose of this paper is to suggest a formalism, which at this point is very crude, with the hope that it can be tested as well as refined. We have purposely exercised some license in providing rationalizations of the existing data in terms of the present model, as if it were a proven theory. These rationalizations suggest the types of refinements which should be looked at. The distribution of k_c and ρ as functions of viscosity contain much useful information. They might ultimately give an explanation for the upward curvature in the high fluidity range which is observed with the present as well as with previous models. Tests of the present model should also be carried out. For example, the rationalization of high slope in the ethane yields from acetyl peroxide suggests that a reactive enough scavenger, present in modest concentration, should be capable of interfering with the ethane formation. Existing data[16] suggests this prediction is incorrect but reinvestigation with other scavengers seems justified. The predictions of the present model with respect to scavange ability of radical pairs are currently being analyzed.

Acknowledgment. We are grateful for the financial support of the National Science Foundation and Professor R. M. Mazo for helpful discussion of this work.

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[16] M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, pp 153–174.

Secondary Deuterium Isotope Effects in Radical-Forming Reactions. III. The Decomposition of Acetyl Peroxide

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Abstract: The α-deuterium secondary kinetic isotope effect on the decarboxylation of the acetoxy radical has been estimated from the ratio of yields of the two isomeric trideuterated methyl acetates formed from decomposition of unsymmetrically trideuterated acetyl peroxide. The estimated isotope effect is 1.09 ± 0.02 for three deuterium atoms. The isotope effects on the over-all decomposition rates have been measured by a new double-labeling technique. These isotope effects are small and appear to be sensitive to changes in temperature and solvent viscosity. They are interpreted in terms of a mechanism in which diffusive separation of the acetoxy–acetoxy radical pair is included.

Our initial interest[1] in secondary deuterium isotope effects in peroxide decompositions arose indirectly from the observation of apparent exchange between the carbon dioxide forming intermediates in the decomposition of labeled acetyl peroxide and added unlabeled acetate ion.[2] Our interpretation of these observations was that the acetoxy radical intermediate produced in the process had a sufficient lifetime to undergo electron exchange with the acetate ion present. Just after the preliminary electron exchange results were first obtained, a report of a study of the heavy atom isotope effects on the decomposition of this peroxide was published.[3] The conclusion from this study was that this reaction was a "concerted" process involving C–C as well as O–O bond breaking. We thus felt that the deuterium isotope effect should be examined as a method for choosing between these apparently different conclusions as to the mechanism of the decomposition. Initial isotope effect studies, carried out using conventional kinetic techniques, indicated that there was very little if any effect of deuteration on the rate of decomposition of this peroxide; a result which was apparently in accord with expectations for a stepwise mechanism with the intervention of a well-defined acetoxy radical intermediate.

Relatively few radical reactions have been investigated using secondary isotope effects and so we felt it was worthwhile to continue this line of endeavor and examine the isotope effect on the decarboxylation process. It had previously been shown[4] that the methyl acetate product was probably a result of a cage reaction. Thus an estimate of this isotope effect appeared accessible from the determination of the ratio of yields of the two trideuterated methyl acetates which could be formed from the trideuterated peroxide. The results of these experiments are detailed below.

During the course of this work, it was elegantly demonstrated[5] that the decomposition of acetyl peroxide involves the *reversible* formation of acetoxy radicals

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[1] W. D. Brewer and T. Koenig, *Tetrahedron Letters*, 2773 (1965).

[2] W. D. Brewer, unpublished results in these laboratories; T. Koenig and R. Wielesek, submitted for publication.

[3] M. Goldstein, *Tetrahedron Letters*, 1601 (1964).

[4] L. Herk, M. Feld, and S. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

Table I. Mass Spectral Results[a]

Sample	m/e 80	77	74	62	59	Results
$CH_3CO_2CH_3$			1.00		0.396	0.396[b]
$CD_3CO_2CD_3$	1.00			0.349		0.349[c]
Mixture A[d]				1.000	0.558	0.636[e]
Mixture B[f]				1.000	0.702	0.643[e]
1[g]	0.0326	1.000	0.0317	0.237	0.168	1.08[h]
2[g]	0.1222	1.000	0.1872	0.223	0.201	1.11[h]
3[g]	0.0957	1.000	0.1117	0.256	0.20	1.11[h]
4[g]	0.0708	1.000	0.0566	0.240	0.178	1.13[h]
4[i]	0.0714	1.000	0.0533	0.224	0.165	1.13[h]
5[g]	0.2138	1.000	0.1229	0.29	0.201	1.10[h]
5[i]	0.1821	1.000	0.1100	0.260	0.180	1.09[h]
Av[g]						1.11
6[j]	169.8	0	213.4			(1.00)
6[k]	169.9	0	219.8			1.03[l]

[a] Mass spectral peak intensity ratios in arbitrary units. [b] Correction factor for the 59 peak due to the 74 peak. [c] Correction factor for the 62 peak due to the 80 peak. [d] A mixture containing methyl acetate-d_3 and methyl-d_3 acetate in a mole ratio of 1.19/1.09. [e] Ratio of molar sensitivity factors for the 59 and 62 peaks. [f] A mixture containing methyl acetate-d_3 and methyl-d_3 acetate in a mole ratio of 1.57/0.79. [g] Methyl acetate mixture collected from decomposition of unsymmetrical peroxide decomposed in isooctane at 74.8°. [h] Apparent ratio of yields of methyl acetate-d_3 and methyl-d_3 acetate. [i] Methyl acetate mixture from unsymmetrical peroxide decomposed 80% at 74.8°. [j] Methyl acetate mixture from the decomposition of acetyl peroxide and acetyl peroxide-d_6 in isooctane. [k] Methyl acetate mixture from decomposition of acetyl peroxide and acetyl peroxide-d_6 in paraffin oil at 74.8°. [l] Ratio of 74/80 ratio in isooctane to paraffin oil.

since the oxygen atoms of the peroxide are equilibrated at rates comparable to the over-all reaction. We have recently proposed[6] a general model for the behavior of reactive radical pairs which allows the inclusion of a diffusive separation step of acetoxy radical pairs, in competition with geminate combination or decarboxylation, in the over-all scheme. Such a scheme easily accounts for the recombination as well as viscosity effects on the over-all rates[7,8] of destruction of acetyl peroxide. This scheme can also be used in the analysis of the expected isotope effects on these rate constants.

The conventional kinetic techniques employed in the original study could not possibly give results accurate enough to test these models. A method which we hoped would suffice for this purpose is outlined in Scheme I. The method consists of decomposition of samples of deuterated and oxygen-18-enriched protio peroxide for short and infinite reaction times; collection and oxygen-18 analysis of the carbon dioxide produced in each case. Then a mixture of the two is treated similarly. The ratio of yields (y^*/y) of the carbon dioxide from the two peroxides is related to the rate constants by

$$\frac{y*}{y} = \frac{n^*P_0^*(1 - e^{-k^*t})}{nP_0(1 - e^{-kt})} \qquad (1)$$

where, n and n^* are efficiencies of carbon dioxide which correct for the ester formation, P_0^* and P_0 are initial peroxide concentrations. After power series expansion, (2) is obtained (for short times). The composition of a

$$\frac{k^*}{k} = \frac{(y^*/y)_0}{n^*P_0^*/nP_0} = \frac{(y^*/y)_0}{(y^*/y)_\infty} \qquad (2)$$

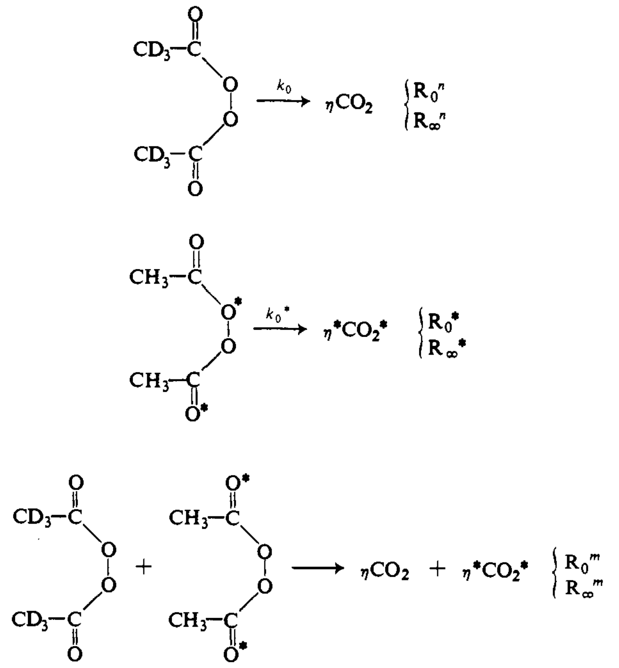
sample of carbon dioxide which results from an enriched and nonenriched source can be analyzed according to (3)

$$\frac{N^*}{N} \quad \left(\frac{R^m - R^n}{R^* - R^m}\right)\left(\frac{1 + R^*}{1 + R^n}\right) = \frac{y^*}{y} \qquad (3)$$

where N^* is the mole fraction of carbon dioxide from the enriched sample and N is the mole fraction of carbon dioxide from the normal abundance sample. The fraction $n^*P_0^*/nP_0$ can be obtained from (3) using the carbon dioxide samples from infinite reaction time and the rate ratio in terms of the 46/44 mass spectral peak intensity ratios becomes

$$\frac{k_0^*}{k_0} = \left(\frac{R_0^m - R_0^n}{R_0^* - R_0^m}\right)\left(\frac{R_\infty^* - R_\infty^m}{R_\infty^m - R_\infty^n}\right) \qquad (4)$$

Scheme I



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(5) (a) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (b) J. C. Martin and S. Dombchik, "Oxidation of Organic Compounds-I," Advances in Chemistry Series No. 75, American Chemistry Society, Washington, D. C., 1968, p 269.

(6) T. Koenig, submitted for publication.

(7) W. Braun, L. Rajbenbach, and F. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(8) W. Pryor and K. Smith, *J. Am. Chem. Soc.*, **89**, 1741 (1967).

Table II. Double-Labeling Results[a] at 74.8°

Peroxide	R_0^n	R_∞^n	R_0	R_∞	R_0^*	R_∞^*	k_0/k_0'	$(k^{16}/k^{18})^{n\,b}$	$(k^{16}/k^{18})^{*\,c}$	n^*/n
A[d]	0.505	0.515	1.105	1.115	1.692	1.728	1.044	1.020	1.021	1.000
A[e]	0.505	0.514	1.110	1.113	1.702	1.729	1.051	1.018	1.016	0.994
B[d]	0.502	0.513	1.077	1.090	1.625	1.658	1.033	1.022	1.020	0.994
B[e]	0.503	0.511	1.091	1.093	1.631	1.660	1.061	1.016	1.018	1.004
B[f]	0.500	(0.511)	1.093	(1.093)	1.629	(1.660)	1.078	1.022	1.019	(1.004)
Av[d]							1.039	1.021	1.020	
Av[e]							1.056	1.017	1.017	

[a] R's reported as 46/44 ratio × 100. [b] Oxygen-18 isotope effect for the deuterated compound. [c] Oxygen-18 isotope effect for the oxygen-18-enriched compound. [d] Isooctane. [e] Paraffin oil. [f] Paraffin oil 60°. Only the short-time samples were measured at this temperature.

where the subscripted R's refer to short and infinite reaction times and the $1 + R$ terms have been cancelled to sufficient accuracy.

Results

Unsymmetrical Peroxide Decomposition. Authentic samples of the two unsymmetrically trideuterated as well as perdeuterated methyl acetates were first synthesized and their mass spectra recorded. The results of these measurements (Table I) showed that the 59/62 peak intensity ratio could be used for the analysis required since the 62 peak is unique for the alkyl-deuterated compound and the 59 peak is unique for the acyl-deuterated compounds. Controls were then carried out to determine if a mixture of the two could be isolated and analyzed reproducibly. Authentic mixtures were subjected to several passes through the gas chromatograph and the 59/62 peak intensity ratios were not altered. One sample was divided into two portions. One portion was injected and the first half of the glpc peak collected. The second portion was injected and the second half of the glpc peak collected. These gave identical 59/62 ratios. We thus felt that isotopic separation during the purification procedure was not a problem. We also investigated the sensitivity of the 59/62 ratio to instrumental settings and sample system pressures. No significant variations were found over the usual range of conditions.

Initial attempts to produce trideuterated acetyl peroxide from solutions of peracetic acid and acetic anhydride were singularly unsuccessful. Material which was close to 50% deuterated (by nmr using dioxane as an integration standard) was obtained using peracetic acid[9] which was distilled into chloroform and treated with acetyl chloride-d_3 and 2,6-lutidine for a short time at −20°. The mass spectra of the methyl acetate mixture, obtained from the decomposition of such samples, showed that the two symmetrical esters (perdeuterio and protio) were present. The degrees of contamination were quite variable though the two impurities were usually present in nearly equal amounts which would explain the near 50% total deuterium content of the starting peroxide. This could be a result of an equilibration of the peracetic acid with hydrogen peroxide and acetyl peroxide. That these symmetrical esters could not result from bimolecular reactions of the peroxide was verified by decomposition of a mixture of protio and perdeuterio peroxide. The methyl acetate mixture from this decomposition gave a negligible 77 mass spectral peak.

The presence of these contaminants can be corrected for by using the measured 62/80 and 59/74 peak intensity ratios of the authentic symmetrical esters. The data of Table I show the pertinent observed mass spectral peak intensities. Before the yields were obtained from the corrected 59/62 ratio, the ratio of molar sensitivities of the instrument had to be determined. This was done by careful preparation[10] of authentic mixtures of the two unsymmetrical esters. The sensitivity ratios appeared to be accurate to about 1%. Table I contains the final yield ratios for a number of runs in which the amount of contamination varies widely. The ratio of yields in isooctane is 1.11 ± 0.02. The disappointingly large uncertainty is due to our inability to prepare an isotopically pure sample of the peroxide. We have some confidence that the true value is within this range since the last five entries in the table were obtained a year after the first set.

Double-Labeling Experiments. The results of the estimates of the isotope effect on the over-all reaction using the double-labeling method are summarized in Table II. A number of problems had to be surmounted before these data were obtained. First, samples of carbon dioxide, taken from frozen solutions, always contained traces of solvent. Initial attempts to remove these impurities using a silica gel chromatography column[11] built directly into the vacuum system were successful but further controls demonstrated that this procedure provided a mechanism for a small amount of oxygen-18 loss from the carbon dioxide on each pass. It was found that even large amounts of isooctane, added to tank as well as 1.4 atoms % oxygen-18-enriched carbon dioxide, had no effect on the 46/44 ratio. The presence of traces of solvent poses no problem. However, even traces of deuterated methyl acetate could not be tolerated since the base mass spectral peak for this compound is m/e 46.

We finally purified the carbon dioxide samples by gas chromatography using a dibutyl phthalate column. An isotopically enriched sample gave the same 46/44 ratio after several passes. A sample, which gave a known 46/44 ratio, was mixed with deuterated methyl acetate and subjected to this purification. The purified sample gave the same 46/44 ratio as before contamination.

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(9) K. Koubec, M. Haggett, C. Battagia, K. Ibne-Rasa, H. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963).

(10) We are grateful to Ross Christianson and Professor D. F. Swinehart of this department for their assistance in the preparation of gas mixtures with sufficient accuracy using a device designed for their thermal conductivity studies.

(11) M. Goldstein and G. L. Thayer, *J. Am. Chem. Soc.*, **87**, 1933 (1965).

The oxygen-18 content of the carbon dioxide samples from the deuterated peroxide were greater than natural abundance. The deuterated acid, used in their synthesis, was converted to carbon dioxide in a combustion train[12] and the product was found to have a similar isotopic content. This is probably an artifact of the isotopic content of the material used in the manufacture of the deuterated acid.

After these difficulties were realized several runs were attempted using one ampoule corresponding to each of the six required ratios. The short-time samples were analyzed together on one day and the infinity samples the next. The results obtained in this way were in qualitative agreement with the data of Table II but with a larger scatter. This was considered to be due to the memory effects which accumulate in the various stages of purification and analysis of carbon dioxide samples of widely different isotopic content.

Each entry in Table II is the result of the complete analysis of three identical samples. Six $R_\infty{}^n$ infinity samples (three Nujol and three isooctane) were completely analyzed as one set. Since the isotopic contents of the samples are similar, the memory effects are minimal. Next, six $R_\infty{}^*$ samples were run as a set and so on. Two different batches of peroxides were used (A and B).

The results listed reflect the total reproducibility of the experiment. Checks on reasonability of the results are the oxygen-18 isotope effects and the values of n^*/n which seem quite reasonable. The uncertainty in the ratios listed are less than 0.002 for the R^n's and 0.003 for the R^*'s. Calculated average deviations in k_0/k_0' using these values, are ± 0.02. Instrumental corrections cancel from eq 4, to the extent that they are constant. Constancy in tank carbon dioxide readings was observed during the span of each of the sets of data in Table II.

Galvinoxyl Kinetics. The first-order disappearance[13] of galvinoxyl in the presence of decomposing acetyl peroxide was also reinvestigated with the hope that an independent check on these isotope effects might be obtained. The results in isooctane and paraffin oil containing 20% isooctane are shown in Figure 1. The rate plots do appear to be quite linear but the rate constants are considerably smaller than those found earlier by Brewer. More significantly the n value (moles of galvinoxyl decolorized per mole of peroxide) in isooctane is 2.4. Though the blank galvinoxyl–isooctane mixture does appear to be reasonably stable for over 20 hr at this temperature, this value for n precludes conclusions based on these rate constants. The n values of the original study were closer to 2, and the rates were faster so that some other process appears to be occurring which leads to decolorization of galvinoxyl. This causes the apparent first rate constant to be reduced because of the sensitivity of the method to the infinity point. The relative rates in isooctane and Nujol, for what they are worth, are in accord with reversible radical formation.

Discussion

All of the present results confirm the original conclusion, reported in the initial communication,[1] that deuteration has very little effect on the rate of destruction of acetyl peroxide. Operation of the "concerted" mechanism[3] for this process appears unlikely. When the present studies were first considered the best explanation of the over-all sequence appeared to be that proposed by Szwarc[14] (Scheme II) in which the rate-determining step was O–O bond homolysis followed by a series of very rapid steps. With this scheme, the ratio of yields of the two trideuterated methyl acetate products from the unsymmetrical peroxide can be shown to be

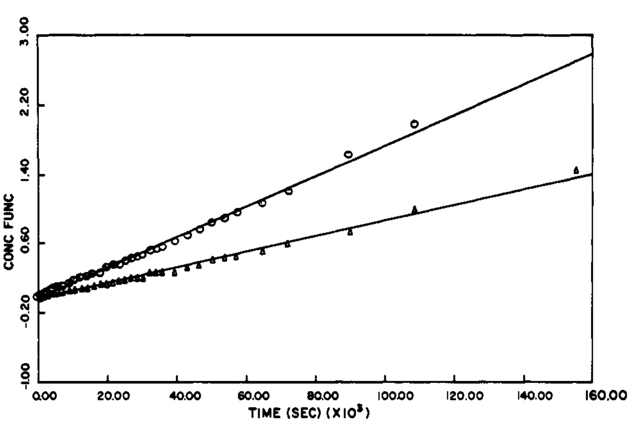
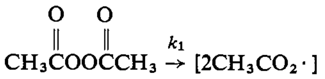


Figure 1. Decomposition of acetyl peroxide in Nujol and isooctane at 74.00°: isooctane, ○; Nujol, Δ.

Scheme II



$$CH_3\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{k_1} [2CH_3CO_2\cdot]$$

$$[2CH_3CO_2\cdot] \xrightarrow{2k_2} [CH_3\cdot\cdot O_2CCH_3]$$

$$[CH_3\cdot\cdot O_2CCH_3] \xrightarrow{k_3} CH_3O_2CCH_3$$

$$[CH_3\cdot\cdot O_2CCH_3] \xrightarrow{k_2} [CH_3\cdot CH_3\cdot]$$

$$\frac{Y_{CH_3O_2CCD_3}}{Y_{CD_3O_2CCH_3}} = \left(\frac{k_3}{k_3'}\right)\left(\frac{k_2}{k_2'}\right)\left(\frac{k_3' + k_2}{k_3 + k_2'}\right) = \frac{y}{y'} \quad (5)$$

where the primed quantities refer to the rate constants (in Scheme II) for the trideuterated species. The measured ratio of yields (Table I) is 1.11 ± 0.02. The isotope effects on k_3 should be negligible since there is probably very little activation energy for this reaction. What isotope effect there is should be due to entropy effects.[15] Therefore, we *assume* $k_3/k_3' = 1$. With this assumption and the yield of methyl acetate (13%), k_2/k_2' is calculated to be 1.09.

Since the rate-determining step of the reaction according to Scheme II is k_1, this value of the isotope effect on k_2 does not necessitate any isotope effect of the over-all rate of destruction of the peroxide. However, the demonstration[5] of reversible acetoxy–acetoxy radical-pair formation perturbs the situation. The reversibility can be formally treated by Scheme II with the simple addition of a k_{-1}.[5a] This does not alter the expression

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[12] T. Koenig and M. Deinzer, *J. Am. Chem. Soc.*, **90**, 7014 (1968).

[13] T. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964); R. C. Lamb, J. C. Pacifi, and L. P. Spadafino, *ibid.*, **30**, 3102 (1965).

[14] M. Szwarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 153.

[15] The reduced rate constant for decarboxylation of the acetoxy radical on deuteration, could result in increasing the average separation of the methyl–acetoxy pairs and therefore reducing the rate of their return.

for the ratio of yields from the unsymmetrical peroxide from (5). The value of k_2/k_2' remains 1.09. The existence of k_{-1} does alter the expression for the rate constant for over-all destruction of the peroxide (k_0, eq 6).

$$k_0 = \frac{2k_1k_2}{k_{-1} + 2k_2} \tag{6}$$

The expression for the over-all isotope effect from this alteration of Scheme II is

$$\frac{k_0}{k_0'} = \left(\frac{k_1}{k_1'}\right)\left(\frac{k_2}{k_2'}\right)\left(\frac{k_{-1}' + 2k_2'}{k_{-1} + 2k_2}\right) \tag{7}$$

where the primed quantities refer to the perdeuterated species. As can be seen, the over-all effect (k_0/k_0') could be near zero even from a fairly significant k_2/k_2' ratio because of the other terms involved. If we assume again no isotope effects on k_1 or k_{-1}, then using the observed[5b,6] fractions return in Nujol and isooctane at 80° and 1.09 for k_2/k_2', one obtains 1.05 and 1.03, respectively, for the ratio k_0/k_0'. These values are in good agreement with the observed values from the double-labeling method under similar conditions (Table II, 1.056 and 1.039). However, a difficulty which we find with this scheme is the way in which it accounts for the apparent increase in return (Figure 5 of ref 6) which occurs with increasing viscosity. The *only step in the forward direction is* k_2 (decarboxylation) and it is not clear how a change in over-all rate[7,8] or fraction return arises without postulating diffusive displacement of some type. The proposed general model of ref 6 is aimed at taking into account the possibility that reactive radical pairs still may undergo diffuse displacement when viscosity is less than infinite. This diffusive model is summarized for the present case in Scheme III.

Scheme III

$$\mathrm{Ac_2O_2} \underset{k_1}{\overset{k_1}{\rightleftharpoons}} [\mathrm{2AcO\cdot}]$$

$$[\mathrm{2AcO\cdot}] \xrightarrow{k_\mathrm{d}} [\mathrm{AcO\cdot \| \cdot OAc}]$$

$$[\mathrm{2AcO\cdot}] \xrightarrow{2k_2} [\mathrm{CH_3\cdot\cdot OAc}]$$

$$[\mathrm{AcO\cdot\cdot CH_3}] \xrightarrow{k_2} [\mathrm{CH_3\cdot\cdot CH_3}]$$

$$[\mathrm{CH_3\cdot\cdot OAc}] \xrightarrow{k_3} \mathrm{CH_3OAc}$$

$$[\mathrm{CH_3\cdot\cdot OAc}] \xrightarrow{k_\mathrm{D}} [\mathrm{CH_3\cdot \| \cdot OAc}]$$

In this scheme we have allowed for diffusive separation of the primary acetoxy–acetoxy pair (k_d) as well as the methyl–acetoxy pair (k_D). The acetoxy–acetoxy pairs which have diffused with respect to primary cage combination are not[6] considered to have been removed from the methyl–acetoxy pair diffusion–combination competition. We must first examine the predictions of this scheme for the relationship of the yields of trideuterated methyl acetates from the unsymmetrical peroxide. This relationship is easily found to be

$$\frac{y}{y'} = \left(\frac{k_2}{k_2'}\right)\left(\frac{k_3}{k_3'}\right)\left(\frac{k_2 + k_3' + k_\mathrm{D}'}{k_2' + k_3 + k_\mathrm{D}}\right) \tag{8}$$

Assuming k_2 to be the only isotopically sensitive step and dividing both numerator and denominator by k_2, one obtains

$$\frac{y}{y'} = \left(\frac{k_2}{k_2'}\right)\left(\frac{1 + (k_3/k_2) + (k_\mathrm{D}/k_2)}{(k_2'/k_2) + (k_3/k_2) + (k_\mathrm{D}/k_2)}\right) \tag{9}$$

In order to extract the value of k_2/k_2' from (9) one needs k_3/k_2 and k_D/k_2. These quantities are given by our[6] general model for diffusive behavior of reactive radical pairs. Figure 5 of ref 6 shows a plot of $(1/y_{\mathrm{CH_3CO_2CH_3}} - 1)$ *vs.* $\sqrt{1/n}$ using the data of Eirich[7] at 60°. The quantity of k_3/k_2 needed in (9) is just the reciprocal of the intercept of that plot ($1/I$). The value of k_D/k_2 is just $[(1/y - 1) - I]/I$ at the required viscosity. Using y/y' of 1.11 and the data of Figure 5 of ref 6 at 60° one obtains 1.09 for k_2/k_2'. The inclusion of an isotopically insensitive diffusive step does not alter the value of the ratio significantly. The accuracy of the values of k_D/k_2 and k_3/k_2 are therefore not very critical.

The ratio of rate constants for over-all destruction of peroxides according to Scheme III is

$$\frac{k_0}{k_0'} = \left(\frac{k_1}{k_1'}\right)\left(\frac{2k_2 + k_\mathrm{d}}{2k_2' + k_\mathrm{d}'}\right)\left(\frac{k_\mathrm{d}' + 2k_2' + k_{-1}'}{k_\mathrm{d} + 2k_2 + k_{-1}}\right) \tag{10}$$

where the primed quantities refer to the deuterated species. Assuming that k_2 is the only isotopically sensitive step and dividing in the numerator and denominator by $2k_2$ gives

$$\frac{k_0}{k_0'} = \left(\frac{k_2}{k_2'}\right)\left(\frac{1 + \dfrac{k_\mathrm{d}}{2k_2}}{1 + \dfrac{k_\mathrm{d}}{2k_2'}}\right)\left(\frac{\dfrac{k_\mathrm{d}'}{2k_2} + \dfrac{k_2'}{k_2} + \dfrac{k_{-1}}{2k_2}}{\dfrac{k_\mathrm{d}}{2k_2} + 1 + \dfrac{k_{-1}}{2k_2}}\right) \tag{11}$$

Evaluation of (11) requires values for $k_{-1}/2k_2$ and $k_\mathrm{d}/2k_2$. The general model[6] and the viscosity effects on over-all rates of disappearance of peroxide or on rate scrambling of oxygen atoms give these ratios. Using the data at 80° in Figure 5 of ref 6 and k_2/k_2' of 1.09, one obtains $k_0/k_0' = 1.009$ in isooctane. This small value of the ratio is due to the additional step (diffusion) in the forward direction which reduces the importance of k_2 in k_0.

Scheme III makes further predictions as to the magnitude of the change in the ratio k_0/k_0' with changing viscosity. The 80° data at Nujol viscosity gives $k_0/k_0' = 1.030$. Both the isooctane and Nujol values are thus predicted to be lower, by Scheme III, than the observed averages reported in Table II (1.039 and 1.057) when all other isotope effects are neglected. However, a value for k_1/k_1' of 1.027 makes the predicted values of k_0/k_0' close to the observed. This same factor is needed to bring the value, predicted for 60° in Nujol (1.059) using the 60° data of ref 6 up to that estimated in Table II (1.078).

A similar situation exists with respect to the heavy atom isotope effects on the decomposition of acetyl peroxide. If we assume, *arbitrarily*, that the carbon-13 isotope effect on k_2 is 4%, then the predicted values for k_0^{12}/k_0^{13} at isooctane and Nujol viscosities and 80° are 1.004 and 1.017, respectively. These are not directly comparable to Goldstein's[3] measured value in isooctane at 45° (1.023) because of the temperature effects on $k_{-1}/2k_2$ and $k_\mathrm{D}/2k_2$. However, a value for k_1^{12}/k_1^{13} of 1.01–1.02

seems to be needed to bring the predicted value into line.

This *rationalization* ($k_1/k_1' > 1$) is attractive to us since it brings the deuterium and heavy atom results into agreement in the sense that both methods indicate some C–C bond reorganization in the formation of the acetoxy radical. Both methods would agree that the formation of the intermediate is "concerted" if by concerted we mean merely perturbation of more than one force constant. Evidence for such a perturbation does not preclude the intervention of an intermediate between one transition state and another transition state involving further perturbation of the same force constant. The reaction is *not* concerted in the more familiar sense of the term (a single-step process with no intervening intermediates). The presence of the acetoxy radical intermediate appears to be unquestionable.[5,12] The suggestion made by this rationalization is that the bonding of acyloxy radicals may not be as straightforward as one might guess.

This ($k_1/k_1' > 1$) is not a unique rationalization of the observed greater magnitudes of k_0/k_0' since there are other isotope effects which have been neglected. The ratio of the yields of methyl acetate and methyl acetate-d_6 from the decomposition of a mixture of acetyl peroxide and acetyl peroxide-d_6 was slightly lower (3%) in Nujol than in isooctane at 75°. Scheme III predicts essentially no change if k_1 and k_2 are the only isotopically sensitive rate constants. Thus, k_d and k_D are probably not absolutely independent of deuteration. For the unsymmetrical peroxide the effect (k_d/k_d') should be very much smaller than for deuterated-protio combinations. In the former case one-half of the radical pair is always deuterated so that there is partial cancellation of effects. Sample calculations indicate that rather large isotope effects (*ca.* 10%) on k_d or k_D would be required to perturb the arguments which we have made. The neglect of the isotope effects on k_3 and k_{-1} could be more serious.[15]

The magnitude of k_2/k_2' is interesting by itself. It is significantly lower than that observed for the closely related β scission of cumyloxy radical ($k/k' = 1.55$).[14] This is expected if the decarboxylation process is highly exothermic as Szwarc[13] has suggested. It is also much smaller than our original values for the α effect in the over-all decomposition of *t*-butyl phenylperacetate and perhydrotropate.

The major conclusions which appear to emerge safely from this study are that the isotope effect on the decarboxylation of the acetoxy radical is 1.09 ± 0.02 for three deuterium atoms. The value of the isotope effect on the over-all process ($k_0/k_0' = 1.039$–1.078 for six deuterium atoms) is in accord with this estimate of k_2/k_2'. We must point out that the uncertainties in our determination of the k_0/k_0' ratios are large enough that the averages for isooctane and Nujol may not reflect any real difference. If taken literally, they seem to be in accord with a model for the over-all process which includes diffusive separation of the acetoxy–acetoxy pair. An alternative is to use the formalism of ref 5 and to postulate that k_{-1} is viscosity sensitive. That is, to make the average value of the rate constant for recombination ($\overline{k_{-1}}$) a function such as

$$\overline{k_{-1}} = \frac{k_{-1}^{\infty} k_{-1}'\eta}{k_{-1}^{\infty} + k_{-1}'\eta} \qquad (12)$$

where $\overline{k_{-1}}$ is the average value of the rate constant for recombination, k_{-1}^{∞} is the rate constant at infinite viscosity and k_{-1}' is the viscosity sensitivity constant. The difficulty with this approach is that it confuses the physical situation, treated by our model,[6] in which the *rate* of combination increases with increasing viscosity due to the increased time the pairs spend together with the situation in which changes in recombination *rate constant* occur for a constant separation of the pair due to changes in solvent viscosity. These distinctions must await further work.

The complexity of the analysis presented here is dictated by the complexity of the problem. We do not consider that the present analysis will be the ultimate one. Rather we believe it is a first approximation to the type which is needed and which appears to be accessible from the proper experiments. Yield and rate data at several temperatures and several viscosities coupled with both deuterium and heavy atom isotope effects could produce a very detailed picture of this process which appears to be much more involved than one would have guessed 2 years ago.

Experimental Section

Proton nuclear magnetic resonance spectra were determined using a Varian A-60 spectrometer. Mass spectra were determined using a modified Consolidated Electrodynamics 26–614 residual gas analyzer. Gas–liquid partition chromatography (glpc) was carried out using an Areograph Autoprep instrument. Visible spectral measurements were made on a Cary 15 spectrophotometer.

Materials. Isooctane was Matheson Coleman and Bell spectroquality that had been refluxed over sodium pellets for 12 hr and distilled at 99.4°. The first fraction of distillate was discarded and the middle fraction collected and stored over molecular sieves. Paraffin oil (white) was obtained from Baker and Adamson and used without further purification. Methyl acetate was purified by glpc on a 20 ft × 0.25 in. column of 10% SE-30 on Chromosorb W.

Acetic acid-d_4 and methanol-d_4 containing 100 ± 1% deuteration by nmr analysis were obtained from Merck and Co. Ltd.

Spectroquality reagent grade chloroform and pyridine from Matheson Coleman and Bell and Mallinckrodt, respectively, were used without further purification, as was the reagent grade 2,6-dimethylpyridine, which was obtained from Aldrich.

Sodium Acetate-d_3. Sodium pellets (1.6 g, 0.070 mol) were slowly added to acetic acid-d_4 (11.1 g, 0.174 mol). The excess acid was distilled under vacuum (0.35 mm) with heating; 14.4 g of sodium acetate was collected. The yield of acetate from acid was 97% of theoretical.

Acetyl chloride-d_3 was prepared by the method of Brown.[16] The yield of acid chloride from d_4 acid was 84% of theoretical.

Acetic Anhydride-d_6. Acetyl chloride-d_3 (10.2 g, 0.126 mol) was slowly added to sodium acetate-d_3 (10.7 g, 0.126 mol) and refluxed for 1 hr. The volatile products were distilled at atmospheric pressure, and the remaining residue was distilled at aspiration pressure with heating. A mixture of acetic anhydride-d_6 and acetic-d_3 acid was obtained in the ratio of 1:3, respectively, by glpc. The mixture was used in subsequent reactions without further purification.

Methyl Acetate-d_6. The acetic-d_6 anhydride–acetic acid mixture (5 ml) and 0.4 ml of methanol-d_4 were refluxed for 2 days. The sample was distilled and purified by glpc. The nmr spectrum showed a trace acetyl peak.

Methyl Acetate-d_3. The acetic-d_6 anhydride–acetic acid mixture (5 ml) and 0.6 ml of methanol were refluxed for 2 days. The sample was distilled and purified by glpc. The nmr spectrum showed 100 ± 2% deuteration of the acyl methyl group.

Methyl Acetate-d_3. Acetic anhydride (2.7 g, 0.025 mol) and methanol-d_4 (0.45 g, 0.0125 mol) were refluxed for 2 days. After distillation the methyl-d_3 acetate was purified by glpc, 0.81 g of the theoretical 0.96 g were collected for a 84.4% yield. The nmr spectrum showed 100 ± 2% deuteration of the ester methyl group.

Acetyl Peroxide-d_3. Peroxyacetic acid was prepared by the

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[16] H. Brown, *J. Am. Chem. Soc.*, **60**, 1325 (1938).

method of Edwards.[9] Stock solutions (2.0 *M*) in chloroform were prepared and immediately used in the acetyl peroxide preparation because the peracid decomposed after several hours.

Acetyl-d_3 chloride (3.4 g, 0.042 mol) in 20 ml of chloroform and 2,6-dimethylpyridine (4.05 g, 0.038 mol) in 20 ml of chloroform were simultaneously added to 20 ml of a peroxyacetic acid (3.2 g, 0.042 mol) solution at 0°. The mixture was stirred for 0.5 hr at 0°.

A kinetic study, in which aliquots of the reaction mixture were iodometrically titrated at certain reaction intervals, indicated that the reaction reached completion after 0.5 hr.

The chloroform solution was washed with 50 ml of a 0.5 *M* sodium carbonate solution, with 50 ml of a 10% hydrochloric acid solution, again with 50 ml of a 0.5 *M* sodium carbonate solution, and finally with 50 ml of distilled water. The chloroform solution was dried over anhydrous sodium sulfate. The peroxide content, as determined by the iodometric titration method of Wagner, Smith, and Peters,[17] was 3.18 g. The yield of peroxide from peracid was 62.4% of theoretical. Nmr analysis using freshly purified, water-free dioxane as an internal standard showed deuterium content near 50%.

The acetyl peroxide-d_3 was crystallized from a *n*-pentane–chloroform mixture at −78°. The peroxide was twice recrystallized from *n*-pentane. After decantation all traces of solvent were removed by pumping on the peroxide crystals under high vacuum while cooling at −78°. Pumping was continued until the mass spectrum of the acetyl peroxide vapor did not contain solvent derived peaks. Gravimetric and titrimetric determinations of peroxide content were reproducible and agreed within 2%. A 0.2 *M* stock solution in freshly distilled isooctane was prepared and stored over molecular sieves.

Acetyl Peroxide-d_6. Hyperol (hydrogen peroxide–urea complex) was prepared by a modified method of Lu, Hughes, and Giguère.[18] The titrimetric peroxide content of the hyperol was 91.5%.

Acetyl peroxide-d_6 was prepared using a modified method of DeTar and Carpino.[19] A kinetic study indicated that the reaction reached completion in 5 hr. The titrametric yield of peroxide from hyperol was 58% of theoretical. Acetyl peroxide-d_6 was purified in the same manner as acetyl-d_3 peroxide. A 0.2 *M* stock solution in freshly distilled isooctane was prepared and stored over molecular sieves.

Acetyl Peroxide-*carbonyl*-^{18}O. Acetyl chloride-^{18}O was prepared by the method of Koenig and Deinzer.[19] Acetyl peroxide-*carbonyl*-^{18}O was prepared by the modified method of DeTar and Carpino[5] as described for the preparation of acetyl peroxide-d_6.

Decomposition of Acetyl-d_3 Peroxide. A typical experiment is described. The peroxide (50 ml, 0.022 *M*) stock solution was placed in a breakseal flask, degassed under high vacuum, sealed, and immersed in a thermoregulated oil bath at 74.0 ± 0.1° for 37 hr. The flask was cooled in an acetone–Dry Ice bath; the seal was broken, and the gases were collected. The reaction mixture was decanted into a flask, and the methyl acetates were concentrated in the isooctane mixture by distillation. The methyl acetates were purified by glpc.

A known mixture of methyl acetates-d_3 was prepared and analyzed by mass spectrometry. An aliquot of this mixture was subjected to the above glpc purification procedure. The first and last halves of the methyl acetate peak were separately collected and analyzed by mass spectrometry. Both samples were identical with the known mixture, such that there was no identifiable isotopic separation on the glpc column. The methyl acetates from the reaction were analyzed by mass spectrometry.

Treatment of Mass Spectrometric Data. The relative amounts of methyl-d_3 acetates and methyl acetate-d_3 were determined from the 62 and 59 peak intensities, respectively. Peak intensity ratios were measurable with an accuracy of 1%. An instrumental sensitivity factor (*S*59/62) was obtained from accurately known gas mixtures of the two methyl-d_3 acetates.[10] Sensitivity factors (*S*77/62 and *S*77/59) for the two individual methyl acetates-d_3 were also determined.

Corrections for the presence of perdeuterio and undeuterated methyl acetate were made as follows. The sensitivity factors (*S*80/62) for perdeuterated methyl acetate and (*S*74/59) for undeuterated methyl acetate were determined. From these the contributions of the perdeuterated methyl acetate to the 62 peak and the undeuterated methyl acetate to the 59 peak could be subtracted. Although the corrections ranged from 6 to 20%, reproducibility of the 62:59 ratio over a number of runs was good to ±2.5%. From the sensitivity factors for the two trideuterated methyl acetates and the corrected 59 and 62 peak heights the parent peak 77 can be calculated and checked for self-consistency. The calculated values agreed with the experimental values to about 1.5%. No corrections were made for mono-, di-, tetra-, or pentadeuteriomethyl acetate because these were present in <1% concentration.

The methyl acetates-d_3 were shown to be formed by a cage mechanism by the following experiment. An equal molar mixture of perdeuterated acetyl peroxide and undeuterated acetyl peroxide was decomposed and the methyl acetates collected and analyzed. Less than 1% of trideuteriomethyl acetate was formed as indicated by the absence of the 77 mass spectral peak.

Decomposition of Acetyl Peroxide-d_6 (AP) and Acetyl Peroxide-*carbonyl*-^{18}O. A typical decomposition in isooctane as solvent is described. Equal volumes of the AP-d_6 (0.182 *M*) and AP-^{18}O (0.186 *M*) were mixed to prepare a stock mixture solution. Three infinity samples were prepared as follows. The mixture of AP-d_6 and ^{18}O (2 ml), 2 ml of AP-d_6, and 2 ml of AP-^{18}O solution were each diluted with 8 ml of freshly distilled isooctane. These were placed in breakseal flasks, degassed under high vacuum, sealed, and immersed in a thermoregulated bath at 74.0 ± 0.1° for 44 hr. Three short reaction time (7% reaction) samples were prepared as follows. The mixture of AP-^{18}O and AP-d_6 (10 ml), 10 ml of AP-d_6, and 10 ml of AP-^{18}O solution were each diluted with 40 ml of freshly distilled isooctane. These were placed in breakseal flasks, degassed under high vacuum, sealed, and immersed in a thermoregulated bath at 74.0 ± 0.1° for exactly 1 hr. The decomposition in paraffin oil as solvent is identical with the decomposition in isooctane except that paraffin oil was used as diluent, and the short reaction time was 2 hr and the infinity time was 88 hr.

All samples were analyzed in the same manner. The flasks were cooled in an acetone–Dry Ice bath, then broken open into a vacuum system under a pressure of approximately 10^{-4} mm Hg. The volatile gases were collected in a tube equipped with a stopcock and frozen with liquid nitrogen, and the noncondensible gases were pumped off. The contents were chromatographed on a 15 ft dibutyl pthalate on Chromosorb column.[20] The CO_2^*/CO_2 was collected and analyzed by mass spectrometry.

A standard sample of CO_2 with 1.83% ^{18}O enrichment was passed over the column several times as was the same sample with methyl-d_6 acetate added. Each sample was analyzed by mass spectrometry. The absolute ^{18}O enrichment did not change within experimental error from the initial value.

Viscosity Determinations. An Ostwald viscometer was used to determine the viscosities of the solvents at two temperatures. 1-Butanol was used as a standard. These data are in Table III.

Table III

Solvent	T, °C	n, CP
1-Butanol	74.1	0.869
Isooctane	74.1	0.443
Isooctane 20% Paraffin oil 80%	74.1	3.990
1-Butanol	60.9	1.124
Isooctane	60.9	0.496
Isooctane–Paraffin oil (20:80)	60.9	7.640

Kinetics of Acetyl Peroxide Decomposition. The pseudo-first-order[13] galvinoxyl method was utilized following the disappearance of galvinoxyl at 763 mμ. Beer's law behavior was determined. The extinction coefficient of the galvinoxyl in benzene was 611. A typical experiment is described. Galvinoxyl (55 mg) and 10 ml of a 4.60×10^{-3} *M* acetyl peroxide solution were diluted to 100 ml in a volumetric flask with freshly distilled isooctane. A 5-ml aliquot was placed in a Pyrex culture tube, degassed under high vacuum,

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[17] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

[18] C. S. Lu, E. W. Hughes, and P. A. Giguère, *J. Am. Chem. Soc.*, **63**, 1507 (1941).

[19] D. F. DeTar and L. A. Carpino, *ibid.*, **77**, 6370 (1955).

[20] We are indebted to Lefford Lowden and Professor D. F. Swinehart for the use of their preparative gas chromatograph.

sealed, and immersed in a thermoregulated oil bath at 74.0 ± 0.1°. The tubes were removed at various time intervals, quenched in ice, read in the spectrometer, and reimmersed in the bath. All rate plots were linear for three half-lives, and the rate constants were obtained by a least-squares treatment[21] of the experimental data. The rate constants were: in isooctane, $k = 1.77 \times 10^{-5}\ \text{sec}^{-1}$ and in paraffin oil, $k = 0.91 \times 10^{-5}\ \text{sec}^{-1}$.

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[21] C. E. Klopfenstein and C. Wilkins, *J. Chem. Educ.*, **43**, 10 (1966).

A Semiempirical Molecular Orbital Method for Estimating the Hyperconjugative Contribution to β-Secondary Deuterium Isotope Effects

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Abstract: A semiempirical equation is derived to connect ω-SCF molecular orbital wave functions and eigenvalues with the hyperconjugative contribution to β-secondary deuterium isotope effects. The results of the application of this equation to a number of hydrocarbon systems are discussed.

Secondary deuterium kinetic isotope effects have been examined as mechanistic probes in relatively few radical reactions. The excellent work of Seltzer[2] in elucidating the detailed mechanisms of azo compound decompositions is the most outstanding example. These effects have also been determined for radical additions to olefins[3,4] but interpretation here is complicated by the simultaneous operation of opposing α and β effects. The β effect has been examined for the formation of the phenethyl radical from both the corresponding azo compound[5] and the corresponding *t*-butyl perester.[6] These values for k_H/k_D, as well as that for the formation of the *t*-butyl radical from *t*-butyl perpivalate,[7] indicate that the β effect for radical formation is much smaller in magnitude than that for formation of cations of the same formal structure.

When we began this work we did not expect that radical isotope effects would be so low. The only β effect for a radical process which had been measured, at that time, was in the autoxidation of cumene.[8] The observed value was comparable to an ionic reaction in that case. After more careful consideration of the general state of the theory of β effects, it was realized that there was little basis for any expectation of the magnitude of such isotope effects. The only factor which resembled a generalization was that these effects were in some way related to hyperconjugation. We therefore carried out a preliminary analysis of the magnitudes of the relative isotope effects in radical- and cation-forming processes predicted by molecular orbital methods. We used the formalism of Salem[9] in this preliminary analysis.[7] The result of this work was that the observed β effects were in good agreement with these preliminary calculations. We thus were encouraged to pursue this line of endeavor more carefully. The additional results are summarized below.

Results

The general formalism[9] used in the preliminary calculations begins with the assumption of a linear correlation of bond distance and π-bond order (eq 1)

$$r = A - BP \qquad (1)$$

where r is the equilibrium bond length, P is π-bond order, A the intercept, and B the slope of the bond order–bond length proportionality. Also, it is assumed that the bond integral can be approximated as

$$\beta = ce^{-r/a} \qquad (2)$$

where c and a are constants. The total bonding potential (V) is assumed to be the sum of π (E) and σ (Σ) parts which are separable (eq 3). With these assumptions one can

$$V = E + \Sigma \qquad (3)$$

integrate the force condition $\delta V/\delta r = 0$ to obtain Σ in

$$\Sigma = \frac{2ce^{-r/a}}{B} - (r - A + a) \qquad (4)$$

terms of π parameters (eq 4). The total potential for an isolated bond is then as shown in eq 5.

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[1] National Defense Education Act Predoctoral Fellow, 1965–1968.

[2] S. Seltzer and F. T. Dunne, *J. Am. Chem. Soc.*, **87**, 2628 (1965); S. Seltzer and S. E. Scheppele, *ibid.*, **90**, 358 (1968); S. Seltzer, *ibid.*, **85**, 14 (1963); S. Seltzer and S. Mylonakis, *ibid.*, **89**, 8598 (1967).

[3] W. A. Pryor, R. W. Henderson, R. A. Patsiga, and N. C. Carroll, *ibid.*, **88**, 1199 (1966).

[4] S. Szwarc, A. P. Stefani, and M. Feld, *ibid.*, **84**, 4451 (1962).

[5] S. Seltzer and E. Hamilton, *ibid.*, **88**, 3775 (1966).

[6] T. Koenig and W. Brewer, *Tetrahedron Letters*, 2773 (1965).

[7] T. Koenig and R. Wolf, *J. Am. Chem. Soc.*, **89**, 2948 (1967); T. Koenig and R. Wolf, *ibid.*, **91**, 2574 (1969).

[8] C. E. Boozer, B. W. Ponder, J. C. Trisler, and C. E. Wightman, *ibid.*, **78**, 1506 (1956).

[9] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966.