atom is present in the labeled 1,3,5-tri-*t*-butylbenzene and that the starting material contains just a minor amount (6%) of the light 1,3,5-tri-*t*-butylbenzene.

Acknowledgment. This research was carried out with the financial support of the Italian Research Council (C.N.R., Rome).

The Decomposition of Acetyl Peroxide in Olefinic Solvents. The Acetyl Peroxide–Cyclohexene Reaction[1]

J. C. Martin,[2] James W. Taylor,[3] and E. H. Drew[4]

Contribution from the W. A. Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois. *Received August 1, 1966*

Abstract: The reaction between cyclohexene and acetyl peroxide, I, yielding cyclohexyl acetate, II, proceeds, contrary to a prior report, with complete scrambling of the oxygen-18 label, initially in the carbonyl group of the peroxide. Four new minor products, the *cis* and *trans* isomers of 2-methylcyclohexyl acetate, III (0.4%), and 1,2-diacetoxycyclohexane, IV (0.9%), are shown also to be formed with complete scrambling of carbonyl label. Failure of added galvinoxyl scavenger to affect the yields of III and IV shows these to be radical-cage products. Cyclohexyl acetate yield is depressed on adding scavenger, suggesting its formation *via* an intermediate radical with a lifetime long enough to allow its escape from the solvent cage. Relative rates of ester formation in competitive reactions for a series of olefins show a qualitative parallel to the π basicities of the olefins, as measured by basicity toward dry HCl, and are consistent with a product-determining reaction of cage acetoxy radicals with olefin to yield a π complex which: (i) in a fast reaction within the solvent cage reacts with the other acetoxy radical to gives IV; (ii) reacts with methyl radical to give III; or (iii), in a subsequent reaction outside the cage, reacts with hydrogen donor to give II.

The thermal decomposition of acetyl peroxide is thought[5] to proceed by simple oxygen–oxygen bond cleavage to yield two acetoxy radicals which decarboxylate with a rate comparable to the rate at which they diffuse apart. Estimates of the lifetime of the acetoxy radical, made from a consideration[6] of the failure to detect typical radical reactions such as hydrogen abstraction by acetoxy radicals, fall in the range 10^{-9} to 10^{-10} sec. From the dependence of the yields of cage products, ethane and methyl acetate, on saturated hydrocarbon solvent viscosity, the rate constant for decarboxylation of acetoxy radical at 60° is calculated[7] to be 1.6×10^9 sec^{-1} (half-lifetime of the acetoxy radical 4.3×10^{-10} sec).

Such a short lifetime for these radicals makes them susceptible to capture only by the most rapid of radical scavenging reactions. For example, attempted[8] trapping of acetoxy radicals by reaction with "moist" iodine solution was not successful, although the intermediacy of the benzoyloxy radical in the thermal decomposition of benzoyl peroxide had been demonstrated by use of this reagent.[9] Rapid hydrolysis of acetyl peroxide makes the method inapplicable in the former case.[8] Addition of the stable free radical galvinoxyl,[8] or diphenylpicrylhydrazyl (DPPH),[8] leads to a reduction in the amount of carbon dioxide evolved from a solution of decomposing acetyl peroxide. Further investigation[10] has shown, however, that although this may reflect scavenging of acetoxy radical it also may result from a direct reaction between acetyl peroxide and the scavenger, at least for DPPH, the scavenger giving the largest effect on carbon dioxide evolution. In general,[11] attempts to scavenge acetoxy radicals before they decarboxylate have been unsuccessful, or at best ambiguous. An outstanding exception to this generalization is the reaction, reported by Shine and Slagle,[12] yielding cyclohexyl acetate from the decomposition of acetyl peroxide in cyclohexene. More than 15% of the acetoxy groups are present as cyclohexyl acetate in the product mixture, an indication of unexpectedly efficient scavenging by cyclohexene, if indeed acetoxy radicals are intermediates in its formation. Cyclopentyl acetate is formed[8] to an even larger degree (*ca.* 30%) when the solvent is cyclopentene.

---

[1] Taken in part from the Ph.D. Theses of J. W. T. and E. H. D., University of Illinois.

[2] Fellow of the Alfred P. Sloan Foundation, 1962–1966; Fellow of the John Simon Guggenheim Memorial Foundation, 1966.

[3] Rohm and Haas Co. Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow, 1963–1964.

[4] Woodrow Wilson Foundation Fellow, 1958–1959; Allied Chemical Corp. Fellow, 1960–1961.

[5] J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.*, **88**, 3650 (1966), and references quoted therein.

[6] L. Herk and M. Szwarc, *ibid.*, 82, 3558 (1960). See also M. Szwarc in "Peroxide Reaction Mechanisms," Interscience Publishers, Inc., New York, N. Y., 1962, p 173.

[7] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962). These calculations involved a derived relationship between the amount of caged products and (viscosity)$^{1/2}$. See, however, an alternative model involving (density/viscosity) (G. Houghton, *J. Chem. Phys.*, **40**, 1628 (1964)) and its application to a consideration of cage products (S. F. Nelsen, and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 143 (1966)).

[8] H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963).

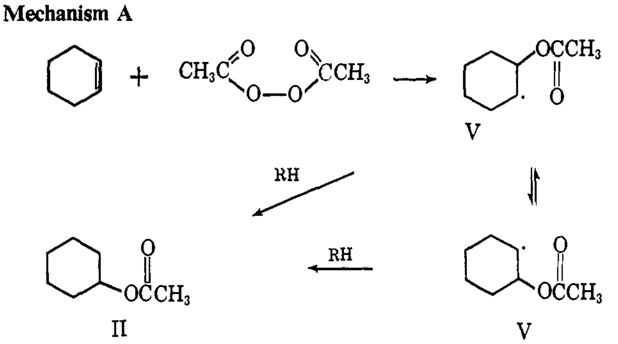
[9] G. S. Hammond, *ibid.*, 72, 3737 (1950); G. S. Hammond and L. M. Soffer, *ibid.*, 72, 4711 (1950).

[10] H. J. Shine, R. E. Spillet, and R. D'Hollander, Annual Report, The Robert A. Welch Foundation, 1964–1965, p 59.

[11] A possible example of a reaction of acetoxy radical with solvent is seen in the decomposition of acetyl peroxide in ^{14}C-labeled acetic acid solvent: A. J. Fry, B. M. Tolbert, and M. Calvin, *Trans. Faraday Soc.*, **49**, 1444 (1953).

[12] H. J. Shine and J. R. Slagle, *J. Am. Chem. Soc.*, **81**, 6309 (1959).

Mechanism A



The unexpectedly large amounts of acetate products formed in olefinic solvent led us[13] to explore the possible importance of a molecule-induced decomposition, a direct reaction between cyclohexene and acetyl peroxide to yield the 2-acetoxycyclohexyl radical (mechanism A). Both intramolecular[14–16] and intermolecular[17] displacements by olefinic groups on peroxidic links have since provided analogies for this postulated mechanism. The results of ^{18}O-tracer studies,[13] which have since been found to be in error (*vide infra*), led us to suggest that at least 38% of the reaction leading to cyclohexyl acetate took this path. Kinetic studies by Shine, Waters, and Hoffman[8] yielded rate constants for acetyl peroxide decomposition which showed sufficiently small variations with solvent changes to rule out mechanism A as the sole or predominant mechanism of decomposition of acetyl peroxide in cyclohexene. (Its operation in all or part of the decomposition events leading to cycloalkyl acetate, which is formed in only 20–30% yield,[8,13] would of course not produce sufficient acceleration of the rate of peroxide decomposition to be readily distinguishable from the other small solvent effects, of the same order of magnitude of importance in the over-all decomposition scheme, which might be invoked to explain the observed[8] changes of rate with solvent.)

The omission of mechanism A from the over-all mechanistic scheme for acetyl peroxide decomposition, in accord with the failure to obtain firm evidence for its operation, leaves us with the problem of explaining the surprisingly efficient addition of acetoxy radicals to cyclohexene, when the comparable addition to styrene,[18] or supposedly facile hydrogen abstractions,[18] are not sufficiently rapid to compete effectively with decarboxylation.

Experimental Section[19]

Reagents. The purification of cyclohexene and the preparation of acetyl-*carbonyl*-^{18}O peroxide have been described.[13] Other olefins were obtained from commercial sources or by standard preparative procedures and were purified by distillation through a 100-cm spinning-band column.

Product Studies. For quantitative studies of the peroxide decomposition products in cyclohexene and isooctane solvents a Micro-Tek GC2500 chromatograph, equipped with a flame ionization detector and a high-current thermal conductivity detector, was calibrated with known blends of the liquid products in the solvent of interest, using two separate columns (10 ft × 0.25 in. o.d.) of Apiezon-L (20%) and diethylene glycol succinate (20%) on Analabs ABS 80–90 mesh. The same calibration curve for the blends was obtained by using a syringe for injection as was obtained by sealing them in a capillary and inserting them into the chromatograph by means of a solid-sampler tube crusher. The gaseous products methane, ethane, and carbon dioxide were chromatographed at 80° using a column of activated silica gel. The calibration was accomplished using a gas-tight syringe. Peak-height measurements were found to be superior to area measurements because of base-line drift at the low sample concentration employed. Known volumes of the solvent containing peroxide were sealed in capillaries, and after ten half-lives or more of the peroxide decomposition at the kinetic bath temperature, the capillaries were inserted *via* the solid-sampler device. After the tube was crushed, the sample was swept by a stream of carrier gas into the analyzing column. Product yields were further determined by the use of chlorobenzene as an internal standard, in addition to the capillary runs using other products as standards. The results were closely comparable.

Parallel analyses of methane, ethane, and carbon dioxide were carried out using vacuum line techniques, equating methane to the fraction not condensible at liquid nitrogen temperatures, and discriminating between ethane and carbon dioxide by absorbing the latter with Ascarite. Concentrations determined in this way agreed with those determined by the chromatographic method.

The reproducibility of the chromatographic measurements was ±2% for all products except methane (±5%) and methylcyclohexane (±20%). (The latter product is seen on the trailing edge of a solvent peak.)

The following products were compared (retention times, infrared spectra, and indices of refraction[20]) with authentic samples prepared by literature methods: *cis*-2-methylcyclohexyl acetate,[21,22] *trans*-2-methylcyclohexyl acetate,[21,23] *cis*-1,2-diacetoxycyclohexane,[20,24] and *trans*-1,2-diacetoxycyclohexane.[20,25] Separations of these materials for use in the tracer studies and competition experiments were affected by gas–liquid chromatography (glpc) on a Wilkens Aerograph Model A90 gas chromatograph using: cyclohexyl acetate, silicone 96 on firebrick; 2-methylcyclohexyl acetate mixture, silicone 96 on Fluoropak; and the *cis*- and *trans*-1,2-diacetoxycyclohexanes, diethylene glycol succinate on Chromosorb W (acid washed). To show that scrambling of label in these esters was not important on the latter column, a sample of *cis*-1,2-diacetoxycyclohexane-*carbonyl*-^{18}O, prepared by treatment of the diol with acetyl-*carbonyl*-^{18}O chloride in ether–pyridine, was passed through the column to give diacetate with 1.30 atom % excess oxygen-18 (in two oxygens). Reduction with lithium aluminum hydride gave *cis*-1,2-cyclohexanediol, mp 96–97.5° after crystallization from carbon tetrachloride, with 0.00 atom % excess oxygen-18. A similar control experiment showed cyclohexyl acetate-*carbonyl*-^{18}O containing, after passage through a column of silicone-96 on firebrick at 155°, 1.36 atom % excess oxygen-18, to be reduced to cyclohexanol containing only 0.11% excess oxygen-18.

Oxygen-18 Analyses. The conversion of ^{18}O-labeled samples to carbon dioxide was carried out by the method of Unterzaucher,[26] as used by Doering and Dorfman,[27] and modified by Denney and Greenbaum.[28] Our original system omitted the bromine–carbon tetrachloride wash section, as suggested by Oita and Conway,[29] in order to reduce isotopic memory effects in the system. With this train certain samples (including cyclohexanol[13] and *n*-amyl ether) were found to give gravimetric oxygen analyses which were too high by 5–10% (relative). These same compounds, when labeled, gave low assays for oxygen-18. This error was found to increase with the age of the combustion tubes but was not related

---

[13] J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1234 (1961).

[14] J. C. Martin and T. W. Koenig, *ibid.*, **86**, 1771 (1964).

[15] T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

[16] R. C. Lamb, F. F. Rogers, Jr., G. D. Dean, Jr., and F. W. Voight, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962).

[17] F. D. Greene, W. Adam, and I. E. Cantrill, *ibid.*, **83**, 3461 (1961).

[18] L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

[19] We wish to thank Mr. J. Nemeth for the microanalytical determinations and the oxygen-18 determinations, Mrs. S. Nanousi for the isotope ratio mass spectral measurements, and Mr. R. Johnson for the infrared and nmr spectra.

[20] M. J. Murry and F. F. Cleveland, *J. Chem. Phys.*, 12, 156 (1954).

[21] G. A. C. Gough, H. Hunter, and J. Kenyon, *J. Chem. Soc.*, 2052 (1926).

[22] W. Huchel and A. Hubele, *Ann.*, **613**, 27 (1958).

[23] A. Skita, *ibid.*, **431**, 1 (1923).

[24] F. V. Brutcher and G. Evans, III, *J. Org. Chem.*, **23**, 618 (1958).

[25] A. Roebuck and H. Adkins, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 217.

[26] J. Unterzaucher, *Chem. Ingr.-Tech.*, 22, 39 (1950).

[27] W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953).

[28] D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957).

[29] I. J. Oita and H. S. Conway, *Anal. Chem.*, **26**, 600 (1954).

to the quartz source. (General Electric clear fused quartz tubing, Type 204, and Thermal American Fused Quartz Co., Vitreosil, provided equivalent results.) The effect was quite reproducible if sample size was maintained constant.[13] Careful purification of cyclohexanol (gas chromatography, distillation) gave material which still showed this anomalous behavior, making unlikely any explanation based on hypothetical contained oxidation products. A minor modification of the apparatus was found to obviate the difficulty. A short (5-cm) section of the quartz combustion tube, just at the entrance to the muffle furnance, was lined with a sleeve of platinum foil. In a train so modified, good oxygen-18 results were obtained for cyclohexanol. Results of an extensive study of factors influencing the accuracy of this method of analysis will be published later by one of us.[30]

All analyses carried out on the modified train were good. We monitored the process for possible malfunction by running gravimetric direct oxygen determinations on the unlabeled compounds at the same time as the labeled samples were analyzed for oxygen-18. As a further control, analyses were carried out on crystalline derivatives of cyclohexanol and 2-methylcyclohexanol, the α-naphthylurethans, prepared in the usual manner[31] from the carbinol and α-naphthyl isocyanate.

Degradation of the acetates for determination of label specificity was accomplished, as previously described,[13] by reduction with lithium aluminum hydride.

Duplicate samples of labeled products were converted into carbon dioxide by the combustion procedure using helium sweep gas. Because of slight memory effects in the mass spectrometer, the results from the second sample have been reported. The carbon dioxide was introduced into a Consolidated Nier isotope ratio Model 21-201 mass spectrometer equipped with dual collectors, and the pressure was adjusted to give a constant ion current on the *m/e* 44 collector. The ratios of the ion currents on the 44 and 46 collectors were obtained by a null procedure similar to the one described by Nier.[32] The calculation of the atom % excess is based on nonrandom distribution of the oxygens in the carbon dioxide[33] from the Unterzaucher combustion. In the equation below, R is the normalized ratio obtained by multiplying the sample ratio, 46/44, by 0.004090/(tank 46/44) and X is 0.00204, the natural abundance of oxygen-18.

$$\text{atom \% excess} = \left[\frac{R(1 - X) - X}{R(1 - X) + 1 - 2X} - X\right] 100$$

If the analysis is desired on a per labeled atom basis, the atom % excess is multiplied by n, where n is the ratio of total oxygens to those labeled.

Competitive Studies in Mixtures of Olefins. In these studies an equimolar mixture of cyclohexene and competing olefin was carefully added to crystalline acetyl peroxide[13] (−80°) to afford a 5–10% solution. After drying the solution over sodium sulfate, half was sealed in a small (16-ml) bomb tube. To the other half of the solution, 9,10-dihydroanthracene was added in 1:1 ratio with the peroxide, and the solution was sealed into a tube. The sealed reaction vessels were heated at 82° for 32 hr, then cooled, opened, and analyzed by glpc. In all cases the saturated acetate products were identified by comparison of retention times with known materials. The terminal olefins gave only *n*-alkyl acetates. In a separate run *exo*-norbornyl acetate was isolated, by distillation, from the reaction of norbornene with acetyl peroxide in benzene solution containing added dihydroanthracene. It was identified by comparison (infrared, glpc) with authentic material.

Detection of Isotopic Scrambling during the Decomposition of Acetyl-*carbonyl*-^{18}O Peroxide. In a single run our analytical method[5,34] was applied to a cyclohexene solution of carbonyl-labeled peroxide (initially 1.443% excess ^{18}O) prepared[13,34] from labeled acetic anhydride (1.448% excess). Peroxide recovered after 9000 sec at 80° showed 1.257% excess carbonyl ^{18}O.

Results

The products of the decomposition of acetyl peroxide (0.135 *M*) in cyclohexene, which are listed in Table I, include two significant, previously unreported products, III and IV. Both were shown by infrared spectroscopy (and IV was shown by gas chromatographic resolution) to be essentially equimolar mixtures of *cis* and *trans* isomers (50 ± 10%). Product yields were determined by gas chromatographic analyses of the unresolved peaks for *cis* and *trans* isomers. For those products reported in both studies, our values are in reasonable agreement with those previously[8,12] reported. Products are also listed for decomposition in isooctane solvent (0.135 *M*). Values for these yields agree well with those reported by Szwarc[18] at lower concentrations of peroxide (0.0013 *M*) in the same solvent.

Table I. Products from the Decomposition of Acetyl Peroxide (0.135 *M*) at 80°, in Isooctane and in Cyclohexene

Product	Product yield,[a] Cyclohexene	Isooctane	Fraction[b] found in presence of galvinoxyl scavenger[c]
Carbon dioxide	1.40	1.76	0.97
Methane	1.05	1.40	0.10
Methyl acetate	0.197	0.20	1.00
Ethane	0.046	0.046	1.00
Acetic acid	0.002	0.002	
Methylcyclohexane[d]	0.015		
Cyclohexyl acetate, II	0.292		0.01
3-Cyclohexenyl acetate	0.050		0.01
2-Methylcyclohexyl acetate, III	0.004		1.00
1,2-Diacetoxycyclohexane, IV	0.009		1.00

[a] Expressed as moles/mole of peroxide. Reproducibility is ±2%, except for methane (±5%) and methylcyclohexane (±20%). [b] In cyclohexene solvent, expressed relative to yields in cyclohexene without scavenger. [c] Galvinoxyl added, 11.1 moles/mole of peroxide, probably not completely dissolved. [d] Identified only from retention time measurements.

The effect of galvinoxyl scavenger, added in excess to a cyclohexene solution, is recorded in the third column of Table I in terms of the fraction of the product seen in pure cyclohexene which is seen in the presence of the added scavenger. The carbon dioxide, methyl acetate, ethane, 2-methylcyclohexyl acetate, and 1,2-diacetoxycyclohexane are seen to be formed by processes not intercepted by added scavenger. Methane, cyclohexyl acetate, and 3-cyclohexenyl acetate are not cage products, since their yields are greatly reduced by added scavenger.

The distribution of label in ester products from acetyl-*carbonyl*-^{18}O peroxide[13] was shown by reducing the acetate to the corresponding carbinol and analyzing it for oxygen-18. In some cases the α-naphthylurethan of the alcohol was analyzed. Product purity was shown by carbon and hydrogen elemental analyses, gas chromatography, and (when possible) melting point comparisons. Results show (Table II) complete scrambling, within our experimental error, for the acetate oxygens in II, III, and IV, isolated from the decomposition of acetyl peroxide in cyclohexene con-

---

(30) J. W. Taylor and I-J. Chen, in preparation, contains a discussion of the reduction of memory effects and also proposes an alternative modification of the combustion train.

(31) R. L. Shriner, R. C. Fuson, and D. Y. Curtin. "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 211.

(32) A. O. Nier, W. R. Eckelmann, and R. A. Lupton, *Anal. Chem.*, **34**, 1358 (1962).

(33) W. G. Miller and L. Anderson, *ibid.*, **31**, 1668 (1959).

(34) To be described more completely in a subsequent publication: J. C. Martin and J. W. Taylor, in preparation.

taining added hydrogen donor, dihydroanthracene. These are conditions expected to decrease the lifetime of the possible intermediate, 2-acetoxycyclohexyl radical, and hence expected[13] to reduce the probability of scrambling of label in that intermediate stage of reaction.

Table II. Distribution of Label in Acetates from Decomposition of Acetyl-*carbonyl*-^{18}O Peroxide in Cyclohexene[a]

	% label				
Acetate	Total ^{18}O[b]	Carbinol	Carbonyl[d]	Ether-O	Carbonyl O
Cyclohexyl acetate, II	1.40	0.68[c]	0.72	48.6	51.4
2-Methylcyclohexyl acetate, III	1.31	0.63[c]	0.68	48.1	51.9
cis-1,2-Diacetoxycyclohexane, IVa	1.38	0.67	0.71	48.6	51.4
trans-1,2-Diacetoxycyclohexane, IVb	1.44	0.68	0.76	47.3	52.7

[a] 0.44 *M* acetyl peroxide in cyclohexene containing 0.52 *M* dihydroanthracene. [b] Excess % oxygen-18, calculated assuming one labeled oxygen per ester function. [c] From analysis of an α-naphthylurethan of the carbinol. In the second case the urethan was recrystallized to mp 155–157° (ethanol). The result therefore probably applies rigorously for one isomer only. [d] By difference.

Although all analyses show a slight predominance of label in the ester carbonyl oxygen, the deviation from statistical distribution of label is too small to interpret as support for the previously postulated[14] molecule-induced decomposition. (The scatter about a value different from 50.0% may, in part, represent the operation of an oxygen-18 kinetic isotope effect.)

The yields of II, III, and IV are essentially independent of the added dihydroanthracene, suggesting that in each case the first step of the process leading to ester occurs within the solvent cage. The drastic decrease in the amount of II formed in the presence of galvinoxyl (Table I) suggests interception of the initially formed intermediate at a later stage.

Competitive studies of acetate formation rates in mixtures of olefins (equimolar binary mixtures) were found to give slightly different values when an amount of dihydroanthracene equivalent to the acetyl peroxide was added to the solution (Table III). The changes were small, however, and do not obscure the trend of 1-alkylethylenes giving smaller amounts of acetate than 1,2-dialkylethylenes. Styrene was very unreactive. In the presence of dihydroanthracene, styrene gave, in the nonvolatile fraction, no discernible acetate peak in the infrared region characteristic of β-arylalkyl acetates (1735–1750 cm^{-1}).[35]

All of the oxygen-18 analyses reported in this work were carried out in the modified apparatus described in the Experimental Section on material giving carbon and hydrogen elemental analyses correct within ±0.2%. Parallel direct oxygen determinations on the compounds for which oxygen-18 results are reported were correct to within ±0.4%.

In a single run the amount of scrambling of carbonyl label observed in acetyl peroxide recovered from solvent cyclohexene after one half-life for decomposition (26.4% scrambling) was very similar to that seen in isooctane solvent in a parallel run (25.0% scrambling).

Table III. Competitive Reactions of 1:1 Olefin–Cyclohexene Mixtures with Acetyl Peroxide, 80°

	Composition of saturated acetate mixtures,[a,b] % cyclohexyl acetate			
Olefin	No added DHA	Added DHA[c]	k_{rel}, acetate formation[c]	Methyl affinity[e]
Pentene-1	85	81	0.24	24.5
Heptene-1	81	79	0.26	25.6
Octene-1	80	81	0.24	
Cyclopentene	49	50	0.99	5.8
Cyclohexene	50	50	1.00	0.9
Norbornene	45	51	0.96	50.2
Styrene		Small[d]	Small	792

[a] Terminal olefins gave *n*-alkyl acetates; cyclic olefins gave unrearranged cycloalkyl acetates; norbornene gave *exo*-2-norbornyl acetate. [b] Ratios of areas of glpc peaks. [c] Dihydroanthracene, equivalent to peroxide, added to mixture. [d] By infrared investigation of the total reaction mixture using styrene as solvent. [e] Ratio of the rate of addition of methyl radical to the rate of H abstraction from isooctane, from the work of Szwarc, 65°: J. Gresser, A. Rajbenbach, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961); R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1952); F. Leavitt, M. Levy, M. Szwarc, and V. Stannett, *ibid.*, **78**, 5493 (1955).

Discussion

The observation of essentially complete scrambling of label in the acetate products, II, III, and IV, derived from the reaction of acetyl peroxide and cyclohexene, requires the intermediacy of a species with equivalent oxygen atoms. While this could be provided within the framework of mechanism A, if equilibration of the two 2-acetoxycyclohexyl radicals, V, by the pictured 1,2-migration of the acetoxy group were rapid relative to H abstraction, or if attack on peroxy and carbonyl oxygens were equally rapid,[36] the simpler explanation would involve the intermediacy of the acetoxy radical in a modification of the scheme of Shine, *et al.*[8,12]

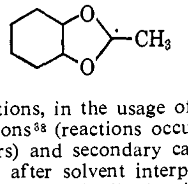
The fact that added dihydroanthracene has no effect on the amount of cyclohexyl acetate, II, formed in the reaction, while galvinoxyl strongly suppresses its formation, is in keeping with the suggested formation of an intermediate within the solvent cage[37] which then, in a much slower step, abstracts hydrogen to give II. The observed reaction of the intermediate in the presence of DHA is hydrogen abstraction leading to II, but galvinoxyl reacts with the intermediate to yield other products.

The formation of minor products III and IV in a reaction unaffected by radical scavengers suggests the

---

(35) This is in keeping with the reported[18] failure to observe any decrease in the carbon dioxide evolved when isooctane was used as the solvent for acetyl peroxide decomposition with added styrene scavenger.

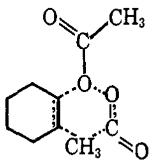
(36) Or if molecule-induced decomposition led directly to



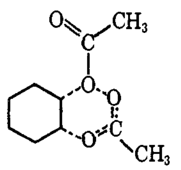
(37) Solvent cage reactions, in the usage of this discussion, include both primary cage reactions[38] (reactions occurring while the partners are still nearest neighbors) and secondary cage reactions[38] (reactions occurring in the interval after solvent interposition between the two partners but before equilibrium distribution in the solvent medium is attained).

(38) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950); *J. Am. Chem. Soc.*, 77, 2042 (1955).

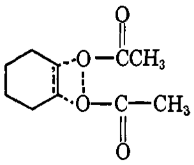
possibility that these products might result from operation of a molecular mechanism.



or



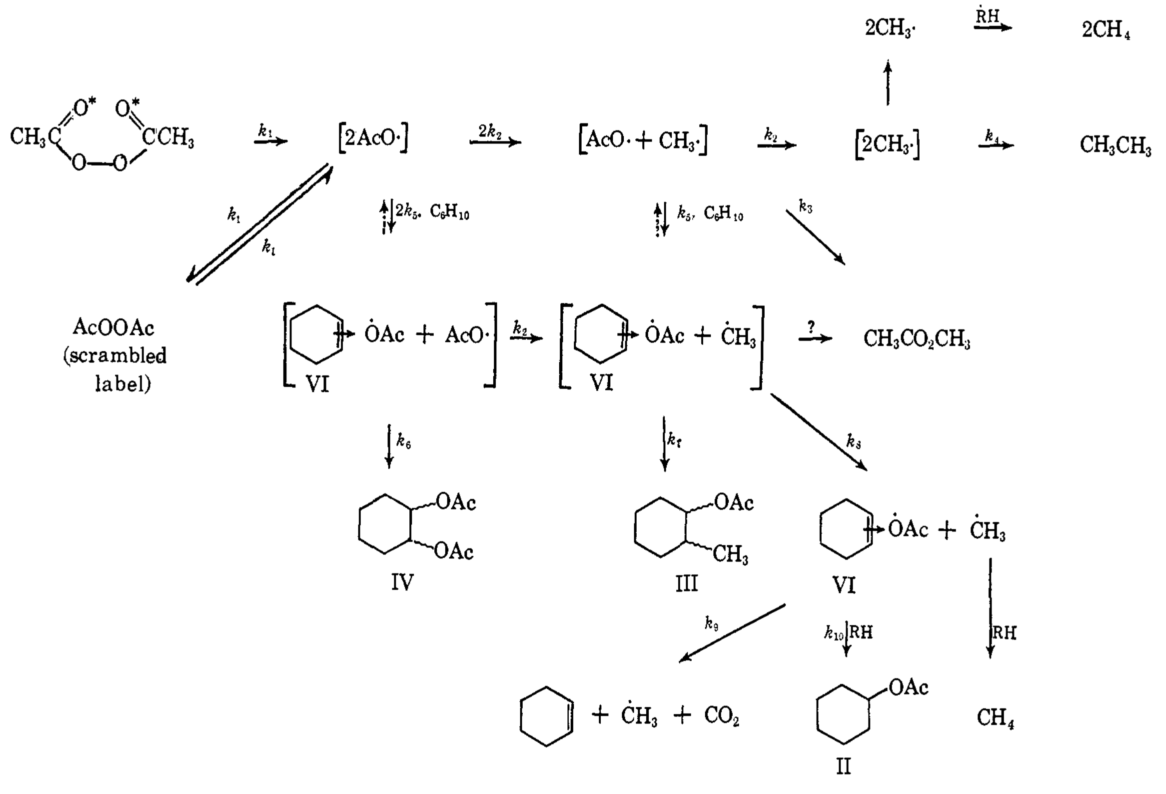
The formation of nearly equal amounts of *cis* and *trans* isomers, with complete scrambling of carbonyl-^{18}O label, however, makes these mechanisms seem unattractive.[39] A two-step mechanism involving molecule-induced reaction leading to V, followed by reaction



with acetoxy radical or methyl radical within the solvent cage, would represent the most efficient possible scavenging of V. The observation of complete equilibration of label in both *cis*-IV and *trans*-IV, therefore, is a very strong argument against equilibration of label by rapid 1,2 migration of the acetoxy group in V.

On the basis of the evidence here described, plus that previously reported, we suggest mechanism B as a possible reaction scheme. The brackets enclose radical pairs, distinguished by being made up of radicals at least 50 times more likely to react with their original partners than with radicals from a different decomposition event. Evidence, based on isotopic tracer studies,[13] for the predominantly intramolecular nature of the process leading from I to methyl acetate and to ethane, together with the failure to obtain unequivocal evidence for scavenging of acetoxy radicals by conventional radicals scavengers, suggests that acetoxy radicals escape the cage only as the complex with cyclohexene. This justifies the omission from mechanism B of arrows representing the diffusion from the cage of free acetoxy radicals from radical pairs of the first two types.

Mechanism B



We represent this complex as a π complex, VI, rather than as the σ complex, V. The rapid formation of a π complex between an electronegative radical Lewis acid, such as the acetoxy radical, and a π-base olefin is not unexpected. Abundant evidence for significant energetic effects of the formation of such complexes with chlorine atom is available.[40] Dramatic effects induced by the presence of mere traces of olefin are seen in reactions of alkoxy radicals[41] and in the cleavage of succinimidyl radical to yield the 3-propionyl isocyanate radical.[42] The rapid decarboxylation seen for the free acetoxy radical might be expected to be much slowed in the π complex.

Mechanism B uses first-order rate constants to describe the probabilities of interconversion of the various radical pairs and of their reactions within the solvent cage. The quantities within the brackets represent well-defined, distinct entities, and the use of first-order rate constants to express the probabilities of reactions of these radical pairs can be useful in comparing rates for the various avenues of reaction open to them. Rates of certain of the reactions (such as k_5 and k_{10})

---

[39] See R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965), for a possible reason for preferring the six-membered cyclic transition state leading to diacetate over the alternative four-ring formulation.

[40] G. A. Russell, *ibid.*, **79**, 2977 (1957); **80**, 4997, 5002 (1958); G. A. Russell, A. Ito, and G. Hendry, *ibid.*, **85**, 2976 (1963).

[41] C. Walling and A. Padwa, *ibid.*, **84**, 2845 (1962); **85**, 1593 (1963).

[42] J. C. Martin and R. E. Pearson, *ibid.*, **85**, 3142 (1963); J. C. Martin and J. H. Incremona, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 5P.

are expressed in terms of pseudo-first-order rate constants, including the unchanging concentration of the reagent solvent. In a simpler case involving decomposition in the less reactive solvent isooctane, product ratios are used[34] to get ratios of these rate constants. Certain rate constants (k_2 and $2k_2$; k_5 and $2k_5$) reflect the statistical factor resulting from the presence of two acetoxy radicals in the first cage pair.

Table III lists relative rates of acetate formation seen in competitive reactions in mixtures of olefins. Competition reactions compare rates of two olefins directly in the same media. This minimizes the uncertainties which plague comparisons of over-all yield of acetate product made from parallel runs in pure olefin solvent. The discrimination resulting from the hydrogen-abstraction step is further reduced in these runs by adding the good hydrogen atom donor dihydroanthracene (DHA) to the medium. This tends to make hydrogen atom availability more nearly constant as olefins are varied, and its addition is seen to have a small effect on the observed relative rates. The biggest effect of added DHA is seen in the medium containing norbornene, which lacks the reactive allylic hydrogens which are available for H-abstraction steps in the other olefins.

The selectivities seen in Table III, even when corrected statistically for the fact that the terminal olefins have only one position for attack by a radical to form a σ complex whereas the internal olefins have two equivalent positions for attack, show very poor correlation with reactivity toward methyl radical (the methyl affinities of Szwarc). In the absence of evidence to the contrary, one might expect the trend of reactivity toward acetoxy radical to parallel that toward methyl radical, at least roughly, if the formation of the σ complex were the reaction being measured in each case. As a matter of fact styrene, the most reactive olefin among those cited in reaction with methyl radical, is least reactive toward acetoxy radical.

A considerably better correlation is seen with basicities toward hydrogen chloride, as reflected in pressure measurements of Brown and Brady.[43] The reaction between hydrogen chloride and olefins is thought to involve formation of a π complex, and the observed order of basicity (monoalkylethylenes < dialkylethylenes < trialkylethylenes) reflects the inductive effects of the substituents. The inductive effect of the phenyl substituent in styrene might be expected to lower its basicity, relative to the other olefins studied, completing the parallel with rates of acetate formation seen in the data of Table III. This suggests that the factors important in the energy of activation for acetate formation are similar to those influencing the π basicity of olefins. Transition states resembling π complexes, which we might visualize, include that for the reaction of olefin and acetoxy radical to form the complex or that for a very exothermic reaction leading from π complex to product.

The possible importance of π-complex formation in the rate-determining step of a radical addition reaction is discounted by Szwarc[44] on the basis that these should be processes with essentially zero activation barriers. His argument suggests the collapse of π complex *via* an activation barrier which is, therefore, rate determining.

The results of our competitive rate studies suggest simply that the product-determining transition state resembles the π complex rather more than it resembles the σ complex. This could be either the transition state for π-complex formation or, more likely,[44] that for the exothermic collapse of the π complex to covalent product. Either rate would reflect primarily the π basicity of the olefinic substrate.[45] The reaction of the π complex could be directly to II, as written, or could involve initial collapse to V, followed by H abstraction. The small but, at least in the case of norbornene, real variation seen in the product ratios of Table III on adding the good hydrogen donor DHA suggests a competition between the final H-abstraction step leading to acetate product (such as k_{10}) and another route (k_9?) leading to destruction of the acetate precursor VI.[46] This competition, which depends on the availability of hydrogen-donor molecules in the medium, may explain the apparent discrepancy between our competitive rates and the product yields of Shine, Waters, and Hoffman,[8] who noted nearly twice as much acetate product in cyclopentene as in cyclohexene. In these experiments[8] the solvent (hydrogen atom donor) was changed along with the substrate. The competitive technique simplifies the interpretation somewhat in that the H-abstraction steps leading to the two product acetates occur in the same medium with the same hydrogen donor availability. The largest effect of added DHA is seen in the case with cosolvent norbornene, a compound lacking a reactive allylic hydrogen-donor site.

The reactions which were included in mechanism B comprise a somewhat arbitrary selection of possibilities. As we have mentioned, the conversion of VI to II may proceed through V, rather than the more concerted process represented by k_{10}. Certain other reactions were omitted from the scheme with good cause. For example, the failure to obtain evidence for the molecule-induced decomposition of 1 provides equally good justification for the omission from the scheme of the microscopic reverse, the reaction of acetoxy radical with VI to regenerate acetyl peroxide. The reaction scheme is suggested as one possible rationalization of the facts now in hand.

The rate of addition of acetoxy radical to the double bond of cyclohexene (*ca.* 10^8 l. mole^{-1} sec^{-1}), which would be required to explain the large amounts of observed acetate products in terms of a direct addition to yield V, is much faster than would be expected on the basis of reasonable analogies.[47] The suggested rapid reaction of acetoxy radical and cyclohexene to form a π complex, which is relatively stable toward decarboxylation, provides a reasonable precursor for the acetate products and does not require that unex-

---

(43) H. C. Brown and J. D. Brady, *J. Am. Chem. Soc.*, 74, 3570 (1952).

(44) M. Szwarc in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 91 ff.

(45) An alternative statement of this view would suggest that methyl radicals, lacking the Lewis acid properties of the more electronegative acetoxy radicals, add to olefins *via* a transition state reflecting quite different properties of the olefin. We may thus rationalize the failure to observe a parallel between the methyl affinities of Szwarc (see footnote *e*, Table III) and the relative reactivities toward acetoxy radicals.

(46) An alternative formulation for a competition which might have this same effect would be that between H abstraction by V and its decomposition to cyclohexene and acetoxy radical (or methyl radical and carbon dioxide).

(47) The rate of radical additions to vinyl monomers is usually $<10^5$ l. mole^{-1} sec^{-1}. See, for example, P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 121.

pectedly rapid radical addition to the double bond be postulated in order to explain the formation of acetate by a route competitive with decarboxylation of the acetoxy radical. The rate expected[44] for π-complex formation might well be rapid enough to compete with decarboxylation of the acetoxy radical,[7,34] a process which is competitive with diffusion from the solvent cage (including secondary recombination[36] as a cage reaction).

Conclusions

These observations seem consistent with the postulate that acetyl peroxide decomposes in solution to give caged acetoxy radicals which can, in reactions competitive in rate with diffusion from the solvent cage, either decarboxylate, react with each other to yield cage products, or react with solvent olefin to form a π complex. The π complex can react with the cage partner radical to give addition products III or IV, collapse to V, or diffuse from the cage and react with hydrogen donors to give II, as outlined in mechanism D.

Acknowledgments. This research was supported in part by a grant from the U. S. Army Research Office, Durham, and in part by a grant from the National Institutes of Health, GM 12290.

Carbonium Ions. I. The Ethylenephenonium Ion

James L. Coke

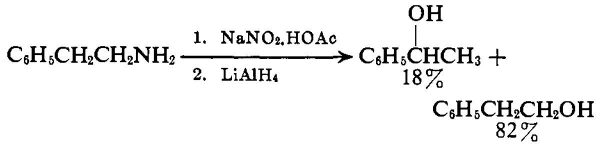
Contribution from the Venable Chemical Laboratory, The University of North Carolina, Chapel Hill, North Carolina.

Received September 17, 1966

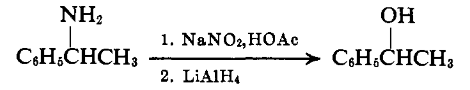
Abstract: The reaction of 2-phenylethylamine with nitrous acid in acetic acid has been reinvestigated. It has been found that both 1-phenylethyl acetate and 2-phenylethyl acetate are produced in this reaction in a ratio of about 1:4. The same reaction with 2-phenylethylamine-1-^{14}C gives 1-phenylethyl acetate in which 0.23% of the ^{14}C has migrated and 2-phenylethyl acetate in which 27% of the ^{14}C has migrated. These results are interpreted as support for an ethylenephenonium ion which does not open back up to a 2-phenylethyl cation.

A number of workers[1] have investigated the reaction of 2-phenylethylamine with nitrous acid both in acetic acid and in water. None of these workers reported the formation of 1-phenylethanol or its acetate. Roberts and Regan[1c] commented on this rather surprising result. As they pointed out one would expect the 2-phenylethyl cation, produced by decomposition of the diazonium cation, to partially rearrange the more stable 1-phenylethyl cation by hydride migration. This kind of rearrangement has been observed in similar systems.[2] It is unfortunate that all the studies on 2-phenylethylamine were carried out before the advent of vapor phase chromatography.

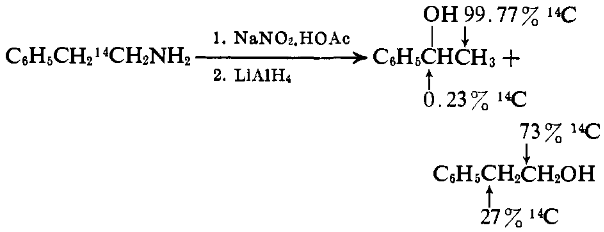
In view of other work we have carried out on rearrangements encountered when primary amines are treated with nitrous acid, we have reinvestigated this reaction on 2-phenylethylamine. Contrary to the observations of earlier workers we have found that rearrangement to give 1-phenylethyl acetate does occur in acetic acid. Evidence for this comes from the following experiment (eq 1). When 2-phenylethylamine was treated with sodium nitrite in acetic acid and the products of this reaction were reduced with lithium aluminum hydride, the alcohol fraction of the product was found to consist of 18% 1-phenylethanol and 82% 2-phenylethanol. The formation of 1-phenylethanol in this reaction has more significance than is apparent since, as will be shown below, it allows one to investigate the nature of an unsubstituted ethylenephenonium ion. When 1-phenylethylamine was treated as above the only product was 1-phenylethanol (eq 2).



$$C_6H_5CH_2CH_2NH_2 \xrightarrow[2.\ LiAlH_4]{1.\ NaNO_2,HOAc} \underset{18\%}{C_6H_5\overset{OH}{\overset{|}{C}}HCH_3} + \underset{82\%}{C_6H_5CH_2CH_2OH} \quad (1)$$



$$C_6H_5\overset{NH_2}{\overset{|}{C}}HCH_3 \xrightarrow[2.\ LiAlH_4]{1.\ NaNO_2,HOAc} C_6H_5\overset{OH}{\overset{|}{C}}HCH_3 \quad (2)$$



$$C_6H_5CH_2{}^{14}CH_2NH_2 \xrightarrow[2.\ LiAlH_4]{1.\ NaNO_2,HOAc} C_6H_5\underset{0.23\%\ ^{14}C}{\overset{OH}{\overset{|}{C}}}H\overset{99.77\%\ ^{14}C}{C}H_3 + C_6H_5\underset{27\%\ ^{14}C}{C}H_2\overset{73\%\ ^{14}C}{C}H_2OH \quad (3)$$

We have repeated earlier work on the deamination of 2-phenylethylamine-1-^{14}C and have separated the products in order to check the location of ^{14}C in each product formed (eq 3). The method used was to carry out the deamination by addition of sodium nitrite to an acetic acid solution of the amine. The mixture of crude esters and alcohols isolated from this reaction was then reduced with lithium aluminum hydride and separated by gas chromatography. The alcohols were converted to their phenylurethans in order to purify them rigorously. The exact per cent ^{14}C at each position was determined by oxidation of each compound to benzoic acid. The radioactivity data are

---

[1] (a) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934); (b) C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, 31, 761 (1953); (c) J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, 75, 2069 (1953).

[2] D. J. Cram and J. E. McCarty, *ibid.*, 79, 2866 (1957).