O.D.U. at 259 mμ) was ATP; peak VI (353 O.D.U. at 259 mμ) was AP_4.

The crystalline material that separated from the original reaction was recrystallized from dioxane as pale yellow rhombohedrons, m.p. 202–203°, λ_{max}^{MeOH} 286 mμ. Its nuclear magnetic resonance spectrum in deuterated dimethyl sulfoxide[18] showed a benzylic singlet at 262 c.p.s. and two doublets (J = 9 c.p.s. each) centered at 463 and 496 c.p.s., typical of *para*-disubstituted benzenes (four aromatic protons per benzylic proton). This material was identified as *trans*-4,4′-dinitrostilbene oxide (III), lit. m.p.[8] 200–201°.

Anal. Calcd. for $C_{14}H_{10}N_2O_5$: C, 58.74; H, 3.52; N, 9.79; O, 27.95. Found: C, 58.72; H, 3.61; H, 3.61; N, 10.36; O, 28.33.

The Stability of the γ-Methyl Ester of ATP in Pyridine. Chromatographically pure γ-methyl ATP (3 μmoles) was converted into its tributylamine salt and dried by four evaporations with anhydrous pyridine. The final residue was dissolved in dry pyridine (0.5 ml.) and kept at room temperature for 3 days. The solvent was then evaporated and the products were chromatographed on a 0.5 × 20 cm. column of DEAE cellulose (HCO_3^-) using a linear gradient of 200 ml. of triethylammonium bicarbonate (0.005 to 0.40 *M*). Two peaks were obtained, the first being AMP (5%) and the second unreacted starting material (95%). Both products were characterized by paper chromatography in several solvents.

The Stability of ATP in α- and β-Picolines. Three samples of the 4-morpholine N,N′-dicyclohexylcarboxamidine salt of ATP[19] (3 μmoles each) were carefully dried by repeated evaporation with pyridine, and residual pyridine was removed by two evaporations with benzene. The final residues were separately dissolved in anhydrous dimethyl sulfoxide (0.01 ml. each), and pyridine, α-picoline, and β-picoline (0.09 ml.) were added, respectively. The clear solutions were kept at room temperature for 3 days and then separated by ion-exchange chromatography on 1 × 25 cm. columns of DEAE cellulose (HCO_3^-) using linear gradients of 200 ml. of triethylammonium bicarbonate (0.005 to 0.40 *M*). The results are shown in Figure 3. The peaks numbered I, II, and III are ADP, ATP, and AP_4, respectively, as determined by paper chromatography in solvents A, B, and C.

The Reaction of Tripolyphosphate and Excess AMP in Pyridine. The pentasodium salt of tripolyphosphoric acid[20] (3.7 mg., 10 μmoles) was converted into the pyridine salt with Dowex 50 (pyridinium) resin and dissolved in 80% pyridine together with AMP (35 mg., 100 μmoles). Tri-*n*-butylamine (0.1 ml., 0.42 mmole) was added and the clear solution was evaporated to dryness. After four evaporations with 5-ml. portions of pyridine the final residue was dissolved in 0.5 ml. of anhydrous pyridine and kept at room temperature for 3 days. The solvent then was evaporated and the products were chromatographed on a 1.0 × 40 cm. column of DEAE cellulose (HCO_3^-) using a linear gradient of triethylammonium bicarbonate (0.005 to 0.5 *M*). Three ultraviolet absorbing peaks were obtained. Peak I (95 μmoles) was AMP, peak II (6.0 μmoles) ADP, and peak III (1.2 μmoles) ATP. Each peak was identified chromatographically by comparison with standards.

(18) Obtained on a Varian A-60 spectrometer. Chemical shifts are measured in c.p.s. downfield from an internal standard of tetramethylsilane.

(19) This salt was prepared by addition of excess free base 4-morpholine N,N′-dicyclohexylcarboxamidine[9] to a solution of pyridinium ATP in methanol and precipitation with ether. We have shown separately that this material behaves identically with the tributylamine salt in its dismutation behavior in pyridine alone.

(20) A generous gift of the Victor Chemical Works, Chicago Ill.

Communications to the Editor

Cage Recombination of *t*-Butoxy Radicals

Sir:

The bimolecular interaction of alkoxy radicals is of fundamental importance in autoxidation and other free radical reactions.[1-3] For example, termination of autoxidation and hydroperoxide decomposition reactions have been written alternatively as the sequence[1b,4,5]

$$2ROO\cdot \longrightarrow 2RO\cdot + O_2 \quad (1)$$

$$2RO\cdot \longrightarrow ROOR \quad (2)$$

or as a single step[2b,3,6]

$$2ROO\cdot \longrightarrow ROOR + O_2 \quad (3)$$

in which eq. 3 may occur through a cyclic process[6]

$$\begin{array}{l} R{-}O\cdots O{-}R \\ \quad\;|\qquad\;| \\ \quad O{-}{-}O \end{array} \longrightarrow ROOR + O_2 \quad (4)$$

or a cage collapse[2b,5,7]

$$ROOOOR \longrightarrow [RO\cdot O_2\cdot OR]^{cage} \longrightarrow ROOR + O_2 \quad (5)$$

Although dialkyl peroxides have been detected in the products of hydroperoxide decompositions[8,9] and

(1) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapters 9 and 10; (b) p. 505 of ref. 1a.

(2) (a) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963); (b) *Tetrahedron Letters*, No. 24, 30 (1960).

(3) (a) R. Hiatt, J. Clipsham, and T. Visser, *Can. J. Chem.*, **42**, 2754 (1964); (b) R. Hiatt, unpublished data.

(4) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discussions Faraday Soc.*, **10**, 242 (1951).

(5) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

(6) C. A. McDowell and S. Sifniades, *Can. J. Chem.*, **41**, 300 (1963).

(7) W. H. Richardson, *J. Am. Chem. Soc.*, **87**, 1096 (1965).

(8) M. H. Dean and G. Skirrow, *Trans. Faraday Soc.*, **54**, 849 (1956).

(9) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 38 (1965).

Table I. Products of Decomposition of Di-*t*-butylperoxy Oxalate

Run	Solvent	Method	DBPO, *M*	Temp., °C.	η^a	Product yields[c] *t*-Bu_2O_2	*t*-BuOH	Acetone[c]	Isobutylene oxide
1	*n*-Pentane	A	0.093	45	2.20	3.9	94.6	~1	0
2	*n*-Pentane	A	0.11	45	2.20	3.6	95.6	~1	0
3	Benzene	A	0.154	45	5.61	5.5	53.1	40	1.0
4	1:1 Benzene–*t*-butyl alcohol[e]	A	0.14	45	...	4.7	...	38.1	0.9
5	1:1.5 Cumene hydroperoxide–chlorobenzene[e]	C	0.055	45	16[b]	6.8	92	~1	...
6	*t*-Butyl alcohol	A	0.128	45	46[b]	10.0	...	41	1.4
7	Cumene hydroperoxide[f]	C	0.43	45	157[b]	19	79	~1	0
8	1:4.3 Cumene hydroperoxide–Nujol[e]	C	0.10	45	...	40	59	~1	0
9	Nujol	A	0.063	35	~1000	76.8	23.2	~0	0
10	None (molten)	B	...	55	...	2.3	23	73	1.5
11	None (crystalline)[d]	B	...	25	...	0	>50[h]	~0	0

[a] Viscosity in millipoise at 25.0°. Data from "Handbook of Chemistry," 7th Ed., N. A. Lange, Ed., Handbook Publishers, Inc., Sandusky Ohio, 1949, pp. 1621–1625. [b] Determined in this work. [c] Yield of *t*-butoxy groups in the listed product based on total accounted *t*-butoxy groups. [d] Fifty per cent decomposition occurred in 10 days, leaving behind pure DBPO as judged by its infrared spectrum. [e] *A*:*B* means *A* volumes mixed with *B* volumes at 25°. [f] A similar experiment in which excess diphenylpicrylhydrazyl was present gave comparable results. [g] The numbers entered under "acetone" are subject to an error of about ±1% yield due to occasional slight decomposition of *t*-Bu_2O_2 during g.l.p.c. analysis. [h] A second product which was not *t*-Bu_2O_2, acetone, or isobutylene oxide has not been identified.

autoxidations,[5] some evidence against cage combination of acetoxy[10] or *t*-butoxy[11b-d] radicals has led to a widely accepted belief that cage combinations of oxy radicals are unlikely.[2a,9,10,12]

We wish to report definitive evidence for cage combination of *t*-butoxy radicals as a significant pathway in the decomposition of di-*t*-butylperoxy oxalate (DBPO)[11a] in the liquid phase.

$$(CH_3)_3COOCCOOC(CH_3)_3 \longrightarrow \left[(CH_3)_3CO\cdot \; \overset{CO_2}{\underset{CO_2}{}} \; \cdot OC(CH_3)_3\right] \quad (6)$$

$$2(CH_3)_3CO\cdot + 2CO_2 \xleftarrow[(6b)]{\text{diffusion}} \qquad \xrightarrow{\text{cage reaction (6a)}} (CH_3)_3COOC(CH_3)_3 + 2CO_2$$

This decomposition was carried out under a variety of conditions described below and tabulated in Table I.

Pure DBPO, shown to be free of decomposition products, was mixed with weighed amounts of solvents. The resulting solutions were either sealed in evacuated ampoules and decomposed for ten half-lives (A) or partially decomposed while the volatile products were continuously vacuum distilled (B). Decompositions of DBPO in the presence of hydroperoxides were carried out in a closed apparatus or gasometer apparatus[13] in which the volatile products were collected by vacuum distillation after the decomposition (C). The chain length of cumene hydroperoxide decomposition was determined by the rate of oxygen evolution.[13a]

The products of the reaction in runs 1–4 and 6 were determined by injecting the reaction mixtures directly onto a Carbowax 20 column operating at 60 to 100° with injection port temperatures less than 130° (to avoid decomposition of di-*t*-butyl peroxide). Areas and retention times were compared with authentic samples and mixtures. In runs 7–9 the products were combined with a measured quantity of benzene and vacuum distilled away from the less volatile components prior to g.l.p.c. analysis. The percentage of *t*-butoxy groups accounted for was >94% in all runs except 7 and 8, where it was 81 and 35%, respectively. The *t*-butyl peroxide was sometimes identified by its infrared spectrum after g.l.p.c. separation.

Run 5 employed DBPO labeled with ^{14}C in the methyl groups.[13a] Here, the yield of DBP was determined by scintillation counting after isotopic dilution and careful purification by distillation and g.l.c. fractionation.[13a]

A notable feature of Table I is that di-*t*-butyl peroxide (DBP) was a product of all decompositions except that occurring in crystalline DBPO. The amount of di-*t*-butyl peroxide obtained is highly dependent on the nature of the solvent. The effective correlation of the yield of DBP with the viscosity of solvent and especially the 77% yield of peroxide in Nujol strongly suggest that the peroxide results from cage combination of *t*-butoxy radicals.[14]

This interpretation was substantiated by carrying out the decomposition of DBPO in cumene hydroperoxide solutions where *t*-butoxy radicals are rapidly trapped by reaction 7.[2,3,13,15]

$$t\text{-BuO}\cdot + \text{ROOH} \longrightarrow \text{ROO}\cdot + t\text{-BuOH} \quad (7)$$

$$\text{RO}\cdot + \text{ROOH} \longrightarrow \text{ROO}\cdot + \text{ROH} \quad (7')$$

Even under these conditions the yields of DBP were 6.8, 19, and 40% in cumene hydroperoxide (CHP) solutions of increasing viscosity. It is noteworthy that increasing the concentration of the *t*-butoxy radical trap (CHP) *increased* the yield of DBP.

(10) M. Swarc, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 173.

(11) (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960); (b) P. D. Bartlett and T. Funahashi, *ibid.*, **84**, 2596 (1962); (c) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962); (d) P. D. Bartlett and H. Sakurai, *ibid.*, **84**, 3269 (1962).

(12) However, see S. Benson, *ibid.*, **86**, 3922 (1964).

(13) (a) A. Factor, C. A. Russell, and T. G. Traylor, *ibid.*, **87**, 3692 (1965). In this article the yield of di-*t*-butyl peroxide coming from DBPO in *t*-butyl hydroperoxide solutions is shown to be similar to that found in cumene hydroperoxide solutions; (b) T. G. Traylor and C. A. Russell, *ibid.*, **87**, 3698 (1965).

(14) (a) S. Kodama, *Bull. Chem. Soc. Japan*, **35**, 652, 658, 824, 827 (1962). The cage combination of methyl radicals is reported to increase from 76 to 90% when the viscosity is increased from 3 to 31 mp.; (b) I. A. Saad and F. R. Eirich, American Chemical Society, Division of Polymer Chemistry, Preprints, **1**, 276 (1960); (c) D. Booth and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1868 (1960).

(15) J. R. Thomas, *ibid.*, **85**, 2166 (1963), has estimated the rate constant for hydrogen abstraction from hydroperoxides by phenoxy radical to be 10^5 l. mole^{-1} sec.$^{-1}$. The corresponding abstraction by the more reactive *t*-butoxy radical should be even faster.

These findings exclude the possibility of external *t*-butoxy radical combination for the following reasons. Even if reaction 7 were not fast, the subsequent reactions 1, 3, and 7′ constitute a chain in which 8 cumyloxy radicals are made for each *t*-butoxy radical.[3,13a] Therefore an upper limit for the production of DBP by external combination (reaction 2) is only $100(1/9)^2 = 1.3\%$, the remainder being dicumyl peroxide and *t*-butylcumyl peroxide. Because reaction 7 *is* fast,[15] it is unlikely that any of the DBP results from external combination under these conditions. The failure of excess diphenylpicrylhydrazyl to prevent DBP formation further substantiates this conclusion.

We conclude from these experiments that all of the di-*t*-butyl peroxide obtained from DBPO is a product of the cage reaction (6a). The discovery of such facile cage recombination of *t*-butoxy radicals separated by 2 molecules of carbon dioxide has important implications in other reactions producing more intimate pairs of alkoxy radicals (*e.g.*, eq. 5).

The results of investigations of reaction 5 will be reported later.[3b,13a,b]

Acknowledgment. We wish to thank the Committee on Research, Academic Senate of the University of California (T. G. T.), and Stanford Research Institute (R. H.), for financial support and Dr. S. W. Benson for suggesting the use of viscous solutions to demonstrate this cage effect.

R. Hiatt
Stanford Research Institute
Menlo Park, California
T. G. Traylor
Chemistry Department, Revelle College
University of California, San Diego
La Jolla, California
Received May 3, 1965

Thermal Decomposition of *cis*- and *trans*-3,5-Dimethyl-1-pyrazoline

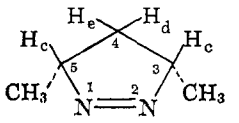
Sir:

Previously we provided kinetic data for 1,3-diradicals as intermediates in the thermal decomposition of 1-pyrazolines.[1] We wish to report further observations on these diradicals.

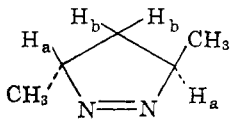
cis-3,5-Dimethylpyrazolidine was prepared by refluxing for 2 hr. 50 g. of *meso*-2,4-dibromopentane[2] in a solution of hydrazine in ethanol. On cooling, the precipitated hydrazine hydrobromide was separated and potassium hydroxide was added. The solids and ethanol were removed to give *cis*-3,5-dimethylpyrazolidine, b.p. 69° (40 mm.); $n^{25}D$ 1.4510; 27% yield. Similarly *dl*-2,4-dibromopentane[2] gave *trans*-3,5-dimethylpyrazolidine, b.p. 69–70° (40 mm.); $n^{25}D$ 1.4580; 57% yield. The pyrazolidines were oxidized[1] to *cis*-3,5-dimethyl-1-pyrazoline (I, b.p. 60–61° (40 mm.), 138–139° (700 mm.); $n^{25}D$ 1.4285) and *trans*-3,5-dimethyl-1-pyrazoline (II, b.p. 60–61° (40 mm.); $n^{25}D$ 1.4347), respectively. Hydrogenation of 3,5-dimethyl-2-pyrazoline over Adams catalyst (70° in methanol) also produces *cis*-3,5-dimethylpyrazolidine.

That the pyrazoline from *dl*-2,4-dibromopentane has the *trans* configuration was demonstrated by the equivalence of the methylene protons on C-4. A 100-Mc. n.m.r. spectrum of II displayed the methinyl protons H_a as a sextet at τ 5.43. The methylene protons H_b appear as a triplet at τ 8.73 (J = 8.5 c.p.s.) and the methyl protons as a doublet at τ 8.71 (J = 7.0 c.p.s.). The *cis* isomer I displayed methinyl protons H_c as a sextet at τ 5.80 and the methyl protons as a doublet at τ 8.46 (J = 7.0 c.p.s.). The C-4 methylene protons form an AB quartet (δ = 164 c.p.s. at 100 Mc. and 96 c.p.s. at 60 Mc., $|J_{e,d}|$ = 12.5 c.p.s.) centered at τ 8.72. Each line was further split into a triplet by the adjacent methinyl protons (J = 8.5 c.p.s.).[3]

The gas-phase decomposition proceeds by first-order kinetics at 220° to produce the products shown in Table I. The pyrazolines were degassed and sealed in ampoules which were heated to 220°, and the ampoules



I



II

were broken directly in the helium stream of a gas chromatograph using a heated bulb crusher. The pressure in the bulbs approximated 1 atm. on completion of reaction. The reaction products were identified by retention times on two columns (a 20-ft. silver nitrate–propylene glycol and an 8-ft. silica gel column) by peak enrichment from authentic samples[4] and by mass spectrometry.

The results indicate that I decomposes through a different diradical species than II, and that I reacts *via* a transition state resembling III to an intermediate having the geometry IV; II similarly through V to produce an isomeric diradical VI.[5] That I goes pre-

Table I. Products of the Thermal Decomposition of I and II

Pyrazolines	1,2-Dimethylcyclopropane[a]		2-Pentene	
	cis	*trans*	*cis*	*trans*
I (*cis*)	33.2 ± 0.6[b]	66.1 ± 0.6	0.0	0.68 ± 0.08
II (*trans*)	72.6 ± 0.4	25.4 ± 0.6	0.92 ± 0.11	1.08 ± 0.17

[a] All products and reactants were checked for isomerization under the reaction conditions. [b] Average deviation as a result of six runs.

(1) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, 87, 3023 (1965).
(2) J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, 28, 1545 (1963).
(3) C. G. Overberger, N. Weinshenker, and J. P. Anselme, *J. Am. Chem. Soc.*, 86, 5364 (1964), have observed similar spectra for *cis*- and *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline. In I the high-field proton (τ 9.50) arises from the shielding of the azo link, indicating that the pyrazoline ring is puckered. See J. J. Uebel and J. C. Martin, *ibid.*, 86, 4618 (1964), for a similar case of shielding by the azo group.
(4) W. von E. Doering and W. Kirmse, *Tetrahedron*, 11, 272 (1960).
(5) Whether the intermediates IV and VI are diradicals or whether