Thermal Decomposition of Some Aromatic Peracetals [αα-Bis(alkyldioxy)-toluenes]

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Four *para*-substituted benzaldehyde peracetals [αα-bis(alkyldioxy)toluenes] have been synthesized along with the parent compound and their rates of thermal decomposition in solution studies. In all cases kinetics which were first order in the peracetal were observed. The decomposition rate was lowered by electron-withdrawing *para*-substituents and increased by electron-donating groups. A reasonable linear Hammett plot was obtained. Some mechanistic aspects on the decomposition of benzaldehyde peracetal are discussed.

THE synthesis of aromatic peracetals [αα-bis(alkyldioxy)-toluenes] was first reported by Dickey and his co-workers.[1] These authors found that when benzaldehyde was treated with excess of t-butyl hydroperoxide in the presence of an acid catalyst a peracetal, αα-bis-(t-butyl-dioxy)toluene (I), was obtained.

The thermal decomposition of an aliphatic peracetal, 2,2-bis-(t-butyldioxy)butane, was examined briefly by Dickey and his collaborators.[2] According to these authors the rates of decomposition of this peracetal were adequately described by first-order equations. An activation energy of 36 kcal mol^{-1} was reported.

In the present work, we have studied the thermal decomposition of benzaldehyde peracetal (I) in solution. The decomposition products were identified. The effect of *para*-substituents on the radical decomposition process of (I) was investigated.

$$p\text{-}XC_6H_4CH(O_2Bu^t)_2$$

(I)	X = H	(IV)	X = Cl
(II)	X = MeO	(V)	X = NO$_2$
(III)	X = Me		

RESULTS AND DISCUSSION

The first-order rate constants derived from the decomposition of peracetal (I) in various solvents are in Table 1. In each instance the fit to a first-order plot was good, although deviation from linearity was sometimes observed at high conversions.†

As may be seen from Table 1, the rates were solvent dependent. The decomposition of peracetal (I) was fastest in di-n-butyl ether and slowest in cumene among the solvents studied.

Using the rate constants tabulated, the energies of activation for the decomposition of peracetal (I) in cumene, dodecane, and n-butyl acetate were calculated from the corresponding Arrhenius equations. In cumene, the value was found to be 31·5 kcal mol^{-1}. It is a reasonable expectation for a homolytic O–O bond cleavage in comparison with those found in the decomposition of t-butyl perbenzoate and benzoyl peroxide.[3-5]

In aliphatic solvents the rates were larger and the energies of activation lower. The same phenomenon was noted by Nozaki and Bartlett [4,5] in the solution decompositions of t-butyl perbenzoate and benzoyl peroxide. Since an ionic reaction of the Criegee type is unlikely to take place in the aliphatic hydrocarbons

TABLE 1

Decomposition of peracetal (I); variation in first-order rate constant with solvent

Solvent	Initial peroxide conc. (M)	Temp. (°C)	10^4 First-order rate-constant (s^{-1})	Activation energy (kcal mol^{-1})
Cumene	0·57	108·5	0·169	
	0·31	108·5	0·171	
	0·15	108·5	0·169	31·5
	0·59	125·6	1·061	
	0·59	135·5	2·602	
Dodecane	0·56	102·6	0·185	
	0·57	111·0	0·347	28·0
	0·56	123·2	1·267	
n-Butyl acetate	0·66	102·6	0·289	
	0·62	112·7	0·797	26·0
	0·64	121·9	1·586	
Di-n-butyl ether	0·48	108·5	0·725	

used in our experiments, our results might be attributable to a similar induced decomposition by the more reactive solvent radicals as proposed by these authors.[5]

The thermal decomposition of peracetal (I) in cumene gave the same first-order rate constants regardless of its initial concentrations (see Table 1). Addition of acrylonitrile, a good radical scavenger for benzoyl peroxide decomposition,[6] did not influence the rate. On the other hand, a rate-depressing effect by acrylonitrile, was noticed in n-butyl acetate solution. These results support our hypothesis that induced decomposition did not occur in cumene where the radicals resulting from the peracetal and solvent would be expected to be equally reactive towards the undecomposed peroxide.[7]

The decomposition products of peracetal (I) in cumene and *p*-xylene are in Table 2. In either case, methane

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† At very high conversions the intensity of the O–O stretching band in the i.r. spectrum, which was used to follow the disappearance of the peracetal, became rather weak with considerable resulting error. Thus the observed deviation at high conversions could be artificial rather than real.

[1] F. H. Dickey, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1949, **71**, 1432.

[2] F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder, and W. E. Vaughan, *Ind. and Eng. Chem.*, 1949, **41**, 1673.

[3] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

[4] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, 1951, **73**, 3412.

[5] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1946, **68**, 1686.

[6] C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

[7] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, 1951, **73**, 3408.

and carbon dioxide were found to be the major products in the vapour phase while the liquid phase consisted chiefly of t-butyl alcohol.

On following the decomposition of peracetal (I) with i.r. spectroscopy, a new band was found at 1765 cm⁻¹ which increased in intensity to a maximum value and subsequently disappeared gradually. This absorption was identical to the carbonyl frequency of t-butyl per-benzoate which is believed to be formed during the initial phase of decomposition. The occurrence of t-butyl perbenzoate as an intermediate is also consistent with the substantial amount of carbon dioxide produced.

These findings in addition to the kinetic parameters described earlier, indicate that the O–O bond cleavage of peracetal (I) probably proceeds in a stepwise rather than simultaneous fashion in both dioxy-groups. We suggest that the initial step involves a homolytic cleavage at a single O–O bond to produce the primary radical (VI) [equation (1)]. The latter would follow a

TABLE 2

Products of decomposition of peracetal (I) at 150°

	In cumene [a]		In p-xylene [b]	
Product	Quantity (mmol)	Mole per mole of (I)	Quantity (mmol)	Mole per mole of (I)
Hydrogen	0·00016	0·0025	0·00013	0·0021
Methane	0·41	0·585	0·158	0·248
Ethane	0·0023	0·0035	0·00002	0·00003
Propane	0·000062	0·000089	0·00002	0·00003
Carbon dioxide	0·173	0·271	0·177	0·278
Isobutene	0·043	0·067	0·036	0·057
Methyl formate	0·0103	0·016	0·011	0·017
Acetone	0·316	0·496	0·272	0·427
t-Butyl alcohol	0·887	1·39	0·957	1·502
Methyl alcohol	0·137	0·215	0·147	0·231
Benzene	0·133	0·208	0·082	0·129
Water	0·030	0·047	0·023	0·036
Benzaldehyde	0·153	0·241	0·215	0·338
Acetophenone	0·250	0·393	0·148	0·233
α-Cumyl alcohol	0·077	0·121		
Benzoic acid	0·024	0·039	0·018	0·028
2,3-Dimethyl-2,3-diphenyl-butane	0·013	0·020		
4,4'-Dimethyl-bibenzyl			0·020	0·031

[a] Quantity of (I) decomposed, 170·7 mg, 0·637 mmol; products unidentified, 18 mg. [b] Quantity of (I) decomposed, 170·7 mg, 0·637 mmol; products unidentified, 17·8 mg.

number of possible reaction pathways leading to the variety of decomposition products obtained.

$$(I) \xrightarrow{\Delta} PhCH(O_2Bu^t)O\cdot + Bu^tO\cdot \qquad (1)$$
$$(VI)$$

The primary radical (VI) may undergo a rearrangement to the t-butyl perbenzoate via the elimination of benzylic hydrogen atom. This reaction takes place most likely while the primary radical (VI) is still in the

cage [equation (2)]. Energy required to break the C–H bond is partially supplied by the formation of O–H bond in the transition state. Subsequent decomposition of the t-butyl perbenzoate would account for the carbon dioxide and benzene found in the decomposition products.[8]

$$(VI) \left[\begin{array}{l} \longrightarrow PhCO(O_2Bu^t) + Bu^tOH \qquad (2) \\ \longrightarrow PhCHO + Bu^tO_2\cdot \qquad (3) \\ \xrightarrow{SH} PhCH(OH)(O_2Bu^t) + S\cdot \qquad (4) \\ \qquad\qquad (VII) \end{array} \right.$$

Rearrangement via the elimination of t-butyldioxyl radical is believed to be an important pathway of the primary radical (VI) in order to account for a number of decomposition products. As illustrated in equation (3) benzaldehyde is produced in this process. The t-butyldioxyl radical eliminated from the primary radical will undergo a variety of reactions with the solvent molecule and other radical species present in the system.[9] When the solvent is cumene, further reactions would lead to the eventual formation of acetophenone and α-cumyl alcohol.[10] Both were found in the decomposition products.

Acetophenone can also be produced from the coupling of a benzoyl radical, generated from benzaldehyde which is a good hydrogen donor, and a methyl radical. We suspect that the acetophenone produced in the p-xylene solution was derived from benzaldehyde in this manner.

Hydrogen abstraction by the primary radical (VI), would result in the formation of a hemiperacetal (VII) as shown in equation (4), where SH is a solvent molecule. Decomposition of (VII) is probably similar to that of hydroxymethyl ethyl peroxide [11] and would produce benzoic acid and t-butyl alcohol. Dissociation of the hemiperacetal (VII) to the original benzaldehyde and t-butyl hydroperoxide is thought unlikely to occur to any significant extent because of an absence of catalysts in our systems.[1,2]

On the basis of these considerations, we suggest that the primary radical (VI) undergoes chiefly three types of reaction as described in equations (2)—(4). These reactions, as estimated from g.l.c. data (Table 2), may account for up to 90% of the decomposition products found in either of the two solvents investigated.

The decomposition of p-methoxy- (II), p-methyl-(III), p-chloro- (IV), and p-nitro-benzaldehyde (V) per-acetals were carried out in cumene. By analogy to their parent peracetal (I) these para-substituted benzaldehyde peracetals also followed first-order kinetics. Our results are in Table 3. The rate of decomposition of the peracetal (I) was lowered by introduction of a p-nitro- or a p-chloro-substituent and accelerated by a p-methyl or a p-methoxy-substituent as would be expected in accord with their electron-withdrawing and -donating

[8] C. Walling, and J. C. Azar, J. Org. Chem., 1968, 33, 3885.
[9] A. V. Tobolsky and R. B. Mescrobian, ' Organic Peroxides,' Interscience, New York, 1954, pp. 91—92.
[10] M. S. Kharasch and A. Fono, J. Org. Chem., 1958, 23, 324; M. S. Kharasch, A. Fono, and W. Nudenberg, ibid., 1951, 16, 105.
[11] E. G. E. Hawkins, ' Organic Peroxides,' Van Nostrand, New York, 1961, pp. 276—277.

power. Such behaviour was also found in substituted t-butyl perbenzoates and benzoyl peroxides.[12,13]

The nature of substituent effects on the thermal stability of peroxides has been attributed to either a

TABLE 3

Decomposition of *para*-substituted benzaldehyde peracetals in cumene with an initial concentration of *ca.* 0·6M

Substituent	Temp. (°C)	First-order rate constant (s⁻¹)	Activation energy (kcal mol⁻¹)
p-MeO	100·0	0·183	
	110·8	0·519	26
	125·5	1·825	
p-Me	100·0	0·103	
	110·0	0·297	27
	126·8	1·142	
p-Cl	100·3	0·072	
	115·1	0·302	30
	126·3	0·941	
p-NO₂	100·8	0·028	
	113·4	0·132	32
	134·9	1·939	

weakening or a strengthening effect on the O–O bond strength.[12,14] The structural dissymmetry of the benzaldehyde peracetals resembles that of t-butyl perbenzoates. The substituent effects would be expected to be somewhat similar in the two systems. Activation energies of the four *para*-substituted benzaldehyde peracetals were calculated from their corresponding Arrhenius equations to be within 26—32 kcal mol⁻¹.

In the Figure the log of the rate constants measured at 100 °C, where k and k_0 are rate constants for the
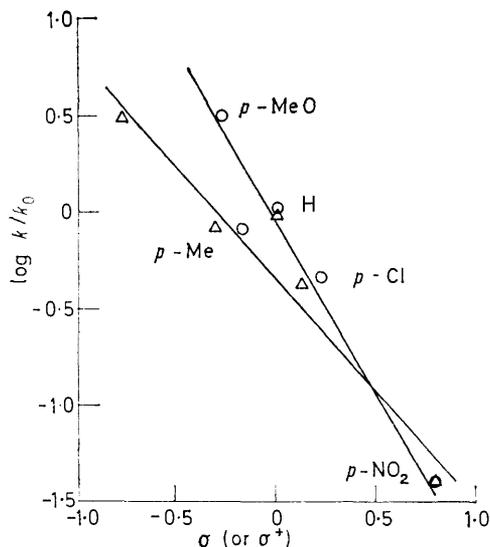
Correlation of rate constants with Hammet's δ (○) and σ^+ (△) values

decomposition of substituted and unsubstituted benzaldehyde peracetals, are plotted against either the Hammett σ or σ^+ values.[15] The fit was fairly good. In this case, ρ was found to be —1·64 and —1·17 re-

[12] A. T. Blomquist and I. A. Berstein, *J. Amer. Chem. Soc.*, 1951, **73**, 5546.
[13] C. G. Swain, W. H. Stockmeyer, and J. T. Clarke, *J. Amer. Chem. Soc.*, 1950, **72**, 5426.

spectively, implying that electron-donating substituents increase the rate of decomposition. Similar effects of *para*-substituents on the rates of unimolecular decomposition have been noted previously in the aromatic perester series.[14]

EXPERIMENTAL

αα-*Bis*-(*t-butyldioxy*)*toluene* (I).—Into a three-necked flask (250 ml), equipped with a mechanical stirrer, addition funnel, thermometer, and an argon inlet, were placed benzaldehyde (25·15 g), t-butyl hydroperoxide (45 g, 90%), and anhydrous calcium chloride (20 g). The mixture was cooled to 5° and concentrated hydrochloric acid (2 ml, 37%) was slowly introduced into the reaction vessel. After standing overnight, the organic layer was separated, washed repeatedly with water, and dried (CaCl₂). The crude product was treated twice with charcoal in hexane. After removing the solvent, a slightly greenish liquid was obtained (25 g, 36%), n_D^{20} 1·4730 (Found: C, 67·0; H, 9·25. C₁₅H₂₄O₄ requires C, 67·15; H, 8·95%), δ (CDCl₃) 1·2 (18H, s, BuᵗO₂), 6·20 (1H, s, PhC*H*), and 7·25 (5H, m, Ph), $\nu_{max.}$ (neat, NaCl) 874m cm⁻¹ (O–O stretching).

The *para*-substituted derivatives (II)—(V) were prepared similarly and gave the anticipated elemental analyses and spectra: (II) m.p. 54—55°, yield 64%; (III) 38—39°, 91%; (IV) 66—67°, 99%; (V) 73—74°, 69%.

Kinetic Measurements.—The decomposition of peracetals was followed by the disappearance of their O–O stretching frequencies (855—880 cm⁻¹) in the i.r. spectrum (in spite of the fact that t-butyl perbenzoate, which was a decomposition intermediate, also absorbed in the same regions, this technique is believed to be useful because of a relatively weak intensity of the perbenzoate band and a comparable rate of decomposition between the latter and its parent peracetal). A Perkin-Elmer 221 model spectrometer and sodium chloride cells were used for the measurements. Solvents were freshly distilled under argon atmosphere. Samples used for kinetic study were placed inside Pyrex ampoules and were sealed under high vacuum after being degassed at liquid nitrogen temperature. A constant temperature bath fitted with a precision temperature controller (±0·1°) was used. Rate constants, activation energies, and ρ values were calculated with regression analysis procedures.

G.l.c. Analysis.—Decomposition products in the vapour phase were analysed with two columns: a 4 ft 5A molecular seive column and a 2 m highly activated silica gel column. The volume of gaseous products generated was measured with a Victor Meyer apparatus. The liquid phase of the decomposition products was also analysed with two columns: a 2·1 m 5% 20 m Carbowax on Teflon 6 and a 2 m Johns–Manville 30 × 60 mesh porous polymer column. Several high boiling fractions including benzaldehyde, acetophenone, α-cumyl alcohol, 2,3-dimethyl-2,3-diphenylbutane, and 4,4′-dimethylbibenzyl were each collected by g.l.c. and were identified by their i.r. and n.m.r. spectra.

[14] R. R. Hiatt, *Canad. J. Chem.*, 1964, **42**, 986.
[15] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.