all prior computations have been performed at point I and along the vertical path from III to II, where disrotary and conrotary ring openings were studied.

The novel pathway I → IV → V → III for the allene oxide–cyclopropanone isomerization has a CNDO/2 barrier of less than 110 kcal/mol, which is less than half that of previously computed CNDO/2 or INDO barriers. No secondary minima were detected in the region near oxyallyl suggesting that, if CNDO/2 is correct, oxyallyl cannot exist as an intermediate as often proposed. It must be admitted, however, that oxyallyl may be a necessary transition state in cycloaddition[15,16] reactions and reactions of allene with ozone.[1] There is one reported isolation of an oxyallyl but for this case the evidence is weak.[17]

The proposed pathway is intuitively quite reasonable in that bending is known to require less energy than bond stretching. Delocalization stabilization in oxyallyl is apparently insufficient to compensate for destabilization due to bond breakage. On the CNDO/2 energy surface, the three-membered ring is preserved intact until bending allows another ring to form with minimal bond stretch. The reliability of this result is hard to assess since CNDO/2 is known to overestimate bond force constants, thereby strongly resisting bond stretching motions, and ring strain may be improperly estimated. Also, the usual uncertainties involving application of semiempirical single determinant SCF schemes apply, and only the closed shell singlet configuration was studied (compare ref 19). Dynamic factors as discussed by Wang and Karplus[18] may also be important, and correlation changes as the conformation is altered from the equilibrium geometry may not be negligible. However, the total error should be much less than the >120 kcal/mol difference between the two paths.

The newly discovered low energy isomerism pathway may shed light on the following. The retention of optical activity when Feist's ester undergoes rearrangement may be more easily explained by a mechanism analogous to that proposed above, than by nonplanar open shell singlet trimethylenemethane[19] or complicated 45° methylene rotations.[20] By completing the upper portion of Figure 1, an analogous pathway may be found for converting I (left) to I (right), which represent different isomers of the product of epoxidation of 1,1-dimethylallene[11,16] or 1,1-di-tert-butylallene.[21] The relative barriers for conversion between cyclopropanone and the two allene oxide isomers would be of interest as well as the relative energy of the three isomers.

In conclusion, the above results illustrate the danger of considering a restricted number of possible reaction pathways. The results indicate that perhaps too much emphasis has been placed on the stability of delocalized configurations. Perhaps, many reaction

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(16) N. J. Turro, Accounts Chem. Res., 2, 25 (1969).
(17) M. H. Fisch and J. H. Richards, J. Amer. Chem. Soc., 90, 1547 (1968).
(18) I. S. Y. Wang and M. Karplus, J. Amer. Chem. Soc., 95, 8160 (1973).
(19) M. J. S. Dewar and J. S. Wasson, J. Amer. Chem. Soc., 93, 3081 (1971).
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(21) J. K. Crandall and W. H. Machleder, J. Amer. Chem. Soc., 90, 7347 (1968).

mechanisms could be profitably reevaluated by considering unusually large distortions of angles (bending) rather than bond stretching. It is hoped that this work will stimulate a check of the proposed mechanism using more accurate and/or more reliable quantum mechanical computational schemes. Spot checking shows that the INDO energy surface is essentially equivalent to the CNDO/2 surface for this system.

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Simultaneous Participation of Three Neighboring Groups in the Transition State for a Radical-Forming Perester Decomposition. A New Route to Hypervalent Compounds of Sulfur and Iodine[1]

Sir:

Several years ago work in these laboratories[2] established the importance of neighboring group participation in the decomposition of ortho-substituted tert-butyl perbenzoates, an effect anchimerically accelerating the decomposition of o-phenylthioperbenzoate (1b) by a

1a, X = H
b, X = SPh
c, X = I

2
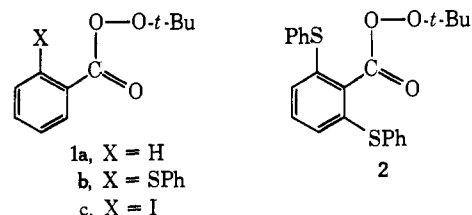
factor of ca. 10^6 (at 0°) relative to 1a. Further work in related systems[3] led us to an unsuccessful search[1a] for evidence for simultaneous participation at both carbonyl oxygen and peroxy oxygen by the two o-thiophenyl substituents of 2; peresters 2 and 1b decompose at about the same rate (Table I).

Recent success in the isolation of stable diaryldialkoxysulfuranes[4] led us to study perester 3a as a possible precursor to sulfurane 5a. We here present evidence for a highly concerted reaction of 3a, simultaneously involving three neighboring groups in a reaction leading through transition state 4a directly to sulfurane 5a and two tert-butoxy radicals.

Perester 3a (mp 44.5° dec) was prepared by treating the corresponding acid chloride with potassium tert-

(1) (a) Part VII of a series on anchimerically accelerated bond homolysis; for Part VI see T. H. Fisher and J. C. Martin, J. Amer. Chem. Soc., 88, 3382 (1966). (b) This is also Part XIII of a series on sulfuranes; for Part XII see J. C. Martin, and E. F. Perozzi, ibid., 96, 3155 (1974).
(2) J. C. Martin and W. G. Bentrude, Chem. Ind. (London), 192 (1959); W. G. Bentrude and J. C. Martin, J. Amer. Chem. Soc., 84, 1561 (1962).
(3) (a) J. C. Martin, D. L. Tuleen, and W. G. Bentrude, Tetrahedron Lett., 229 (1962); (b) D. L. Tuleen, W. G. Bentrude, and J. C. Martin, J. Amer. Chem. Soc., 85, 1938 (1963); (c) T. W. Koenig and J. C. Martin, J. Org. Chem., 29, 1520 (1964); (d) J. C. Martin and T. W. Koenig, J. Amer. Chem. Soc., 86, 1771 (1964).
(4) J. C. Martin and R. J. Arhart, J. Amer. Chem. Soc., 93, 2339 (1971).

Table I. First-Order Decomposition Rates in Chlorobenzene

Compound	T, °C	Concn (M)	$10^5 k$, sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu	k_{rel}, 0°
1a[a]	110	0.02[b]	3.25	33.6	8.2	1
1b[c]	39.7	0.032	10.1	22.3	−5.7	1.1 × 10⁶
3a[d]	12.1	0.02	16.8			
	25.0	0.02	64.5			
	30.0	0.02	107	17.6 ± 0.3[e]	−13.9 ± 0.9[e]	8.9 × 10⁷
	40.0	0.02	309			
	45.0	0.02	444			
1c[c]	85.0	0.031	4.02	28.1	−0.66	3.2 × 10²
3b[d]	68.4	0.02	8.24			
	85.4	0.02	44.5	22.4 ± 0.5[e]	−11.9 ± 1.1[e]	3.9 × 10⁴
	101.6	0.02	168			
2[f]	40.1	0.039	7.07			
10[g]	45.0	10⁻⁴ [h]	2.72	27.9	8.2	3.6 × 10⁴

[a] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3408 (1951). [b] In *p*-chlorotoluene. [c] Reference 2. [d] This work. [e] Uncertainties are standard deviations. [f] Reference 1a. [g] Reference 11. [h] In isooctane.

butyl peroxide at −20°.[5] Its decomposition, followed using the 1772-cm⁻¹ carbonyl stretching frequency in its infrared spectrum, is two orders of magnitude faster than that of **1b** (10⁸ times faster than that of **1a**).

Preliminary product studies show that decomposition of **3a** yields at least 48% of **5a**. Authentic **5a** (mp 186–187°), for nmr, infrared, and mass spectrometric comparisons, was prepared *via* the conversion of 2-bromoisophthalic acid to 2-(phenylthio)isophthalic acid and oxidation of the latter to the corresponding sulfoxide (**6**) by modifications of standard methods.[6,7] Cyclodehydration gives sulfurane **5a** either by pyrolysis of **6** or by its treatment with acetic anhydride–acetic acid.[8]

The formation of radical products *tert*-butyl alcohol (>49%) and acetone (>29%) and the scavenging by galvinoxyl[2] of 50–70% of the expected radicals provide evidence for Scheme I.

The concerted formation of two S–O bonds in transition state **4a** is reflected in the lowering of ΔH^* for **3a** (relative to **1b**) by 4.7 kcal/mol and of ΔS^* by 8.2 eu. Since **3** has two perester functions, while **2** has only one, a statistical factor of 2 is included in the 80-fold acceleration of the decomposition of **3** *vs.* **2**. The "extra" acceleration attributed here to the multiple neighboring group effect in **3** is therefore only a factor of 40 when statistically adjusted. If the statistical factor is used to correct the activation parameters, however, the value of ΔS^* is made more negative by 1.38 eu (R ln 2). The statistically adjusted value of ΔS^*, −15.3 eu, provides an even stronger case for a highly constrained transition state. An extrapolation of the roughly linear relationship between ΔH^* and ΔS^* originally noted by Bartlett and Hiatt[9] places **3** in

(5) Although **3** decomposes rapidly at its melting point we have been unable to cause it to detonate by rapid heating or by striking small samples with a hammer. Large amounts of the material should be handled with the caution which one would exercise with any peroxide, however.

(6) R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957).

(7) H. Gilman and D. L. Esmay, *J. Amer. Chem. Soc.*, **75**, 278 (1953).

(8) Preparation by a similar route of a spirodiaryldiacyloxysulfurane isomeric with **3a** was reported by I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971). Sulfurane **5a**, reported here for the first time, was suggested as a possibly isolable compound in a speculative discussion of sulfurane stabilities by J. I. Musher, *Advan. Chem. Ser.*, No. 110, 44 (1972). Acyclic analogs of **5a**, though not directly observed, were suggested as possible intermediates in nonradical reactions of sulfides with diacyl peroxides by W. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2885 (1972).

(9) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

Scheme I

3a, X = SPh
b, X = I

4a, X = SPh
b, X = I

$2 \, t$-BuO· +

5a, X = SPh
b, X = I
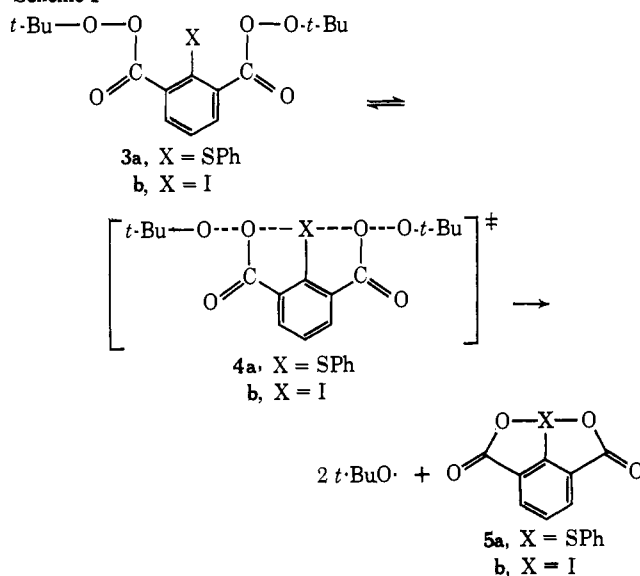
an extreme position consistent with the postulated loss of five internal rotational degrees of freedom on going to transition state **4a**.

The through-bond substituent effect on rate for the substitution of the electron-withdrawing carboxyl group of **3a** for a hydrogen of **1b** would, in the absence of participation, be expected to retard the decomposition of **3a** relative to **1b**.[2] The steric effect of a nonparticipating ortho substituent, on the other hand, might be expected to favor a ground-state conformation with the S-phenyl substituent rotated out of the plane of the isophthaloyl ring, the geometry which has been shown[3b] to be preferred for the kind of participation evidenced for **1b**. The postulation of steric acceleration of a stepwise reaction involving only a single neighboring group interaction is not a satisfactory substitute for Scheme I, however, since the accelerated decomposition of **3a**, relative to **1b**, is a ΔH^* effect, opposed by an unfavorable change in ΔS^*. Furthermore, the iodo substituent of **3b**, with an axial symmetry which rules out this sort of steric effect, provides a closely parallel rate enhancement (a factor of *ca.* 10²) relative to **1c**.

Decomposition of iodoperester **3b** also gives *tert*-butyl alcohol (51%) and acetone (47%) in addition to iodosodilactone **5b**, synthesized earlier *via* another route by Agosta.[10]

(10) W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965).

All evidence points to the mechanism of Scheme I for the decomposition of **3a**. It is interesting to consider this reaction as an analog to the decomposition of di-*tert*-butyl hyponitrite, **10**, studied by Traylor.[11] Both reactions form two *tert*-butoxy radicals, the one with loss of N_2 and the other with loss of sulfurane **5a**. The fact that ΔH^* is 10.3 kcal/mol smaller for the sulfurane reaction suggests several fascinating analogies to the chemistry of azo compounds which are currently being explored.

$$t\text{-BuON}{=}\text{NO-}t\text{-Bu} \longrightarrow 2t\text{-BuO} \cdot + N_2$$
$$\textbf{10}$$
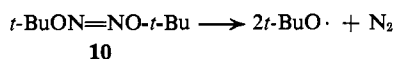
Acknowledgment. We gratefully acknowledge support from National Science Foundation Grant GP 30491X and from National Institutes of Health instrumentation Grants CA 11388 and GM 16864.

(11) T. G. Traylor and H. Kiefer, *Tetrahedron Lett.*, 6163 (1966).

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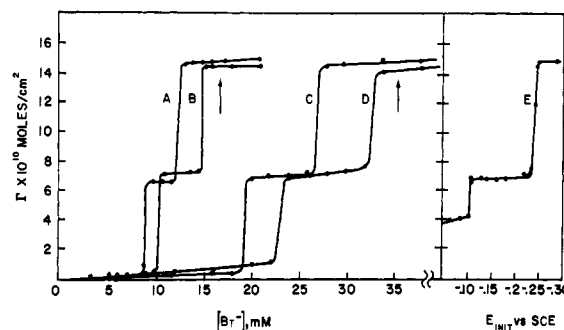*Urbana, Illinois 61801*

Received January 26, 1974

A Crystalline Bilayer Adsorbed on Mercury Electrode

Sir:

There is now substantial evidence[1-3] that the adsorption of Pb^{2+} on mercury electrodes from aqueous halide solutions is controlled by principles quite different from those of anion-induced adsorption.[4] In particular, the surface excess of Pb^{2+} (Γ_{Pb}) exhibits, at a solution [Br⁻] or [I⁻] which is dependent on solution [Pb²⁺] and electrode potential, a sharp increase from a modest to an exceptionally large (plateau) value (*ca.* 8×10^{-10} mol cm⁻²). We have shown[3] that, for a given potential, the discontinuity in Γ_{Pb} occurs for the solution condition $[Pb^{2+}][X^-]^2 = $ constant. We view this adsorption isotherm discontinuity as a surface solubility-controlled formation of a monolayer PbX_2 phase on the mercury surface, *e.g.*, an adsorbed two-dimensional crystal.

This report is a preliminary description of another adsorbing system, Tl^+ in aqueous bromide solution, which exhibits behavior similar to that of Pb^{2+} but in two stages, suggesting the existence of a bilayer surface crystal.

Data for Tl^+ surface excess, Γ_{Tl}, as a function of [Br⁻] are shown in Figure 1 for two [Tl⁺] and two electrode potentials. These adsorption isotherms were obtained by double potential step chronocoulometry[3,5,6] in the usual manner. The distinctive features of the data are the presence of *two* discontinuities, each followed by a plateau in Γ_{Tl}, the second plateau being twice as large as the first. Table I shows that, for a given electrode potential (−0.3 V) in 1 M KNO₃ supporting electrolyte, the solution composition at which each discontinuity in

(1) M. Sluyters-Rehbach, J. S. M. C. Breuksel, K. A. Gijsbertsen, C. A. Wijnhorst, and J. H. Sluyters, *J. Electroanal. Chem.*, **38**, 17 (1972).
(2) A. M. Bond and G. Hefter, *J. Electroanal. Chem.*, **42**, 1 (1973).
(3) H. B. Herman, R. L. McNeely, P. Surana, C. M. Elliott, and R. W. Murray, *Anal. Chem.*, in press.
(4) F. C. Anson and D. J. Barclay, *Anal. Chem.*, **40**, 1791 (1968).
(5) J. H. Christie, R. A. Osteryoung, and F. C. Anson, *J. Electroanal. Chem.*, **13**, 236 (1967).
(6) G. Lauer, R. Abel, and F. C. Anson, *Anal. Chem.*, **39**, 765 (1967).

Figure 1. Surface excess for thallium adsorption from bromide in 1 M KNO₃ at 25°. $E_{final} = -0.70$ *vs.* sce. Data were obtained by double potential step chronocoulometry at a HMDE which was equilibrated with stirred solution for 60 sec: (A) [Tl⁺] = 1.0 mM, $E_{init} = -0.30$; (B) [Tl⁺] = 1.0 mM, $E_{init} = -0.20$; (C) [Tl⁺] = 0.5 mM, $E_{init} = -0.30$; (D) [Tl⁺] = 0.5 mM, $E_{init} = -0.20$; (E) [Tl⁺] = 1 mM, [Br⁻] = 14 mM. Arrows represent bulk solution saturation.

Table I. Adsorption Isotherm Discontinuities for Tl⁺ Adsorption from Bromide Solution at 25° on Mercury at −0.3 V *vs.* sce

Electrolyte	Break	[Tl⁺], mM	[Br⁻], mM	$K_{surp} = $ [Tl⁺][Br⁻]	K_{surp}' [b]
1 M KNO₃[a]	1	5.00	1.96	9.8 × 10⁻⁶	2.82 × 10⁻⁶
	1	2.00	4.6	9.2 × 10⁻⁶	2.71 × 10⁻⁶
	1	1.00	9.5	9.5 × 10⁻⁶	2.82 × 10⁻⁶
	1	0.50	19	10.4 × 10⁻⁶	3.06 × 10⁻⁶
	2	5.00	2.64	13.2 × 10⁻⁶	3.88 × 10⁻⁶
	2	2.00	6.4	12.8 × 10⁻⁶	3.76 × 10⁻⁶
	2	1.00	13.3	13.3 × 10⁻⁶	3.91 × 10⁻⁶
	2	0.50	28.8	14.4 × 10⁻⁶	4.23 × 10⁻⁶
0.1 M KNO₃	1	1.00	3.75	3.75 × 10⁻⁶	3.03 × 10⁻⁶
	2	1.00	5.67	5.67 × 10⁻⁶	4.57 × 10⁻⁶
1 M KF	1	1.00	6.0	6.0 × 10⁻⁶	2.66 × 10⁻⁶
	2	1.00	8.75	8.75 × 10⁻⁶	3.88 × 10⁻⁶

[a] Data are averages of two determinations. [b] Correction of K_{surp} for Tl⁺ bound by supporting electrolyte anion using association constants $K_{TlNO_3} = 2.4$, $K_{TlF} = 1.25$.

Γ_{Tl} occurs is remarkably well described by the relation [Tl⁺][Br⁻] = constant = K_{surp}.

These results, over a tenfold concentration range, leave little doubt that the discontinuities reflect control of Tl⁺ adsorption by the solubility of TlBr at the solution-mercury interface. The surface solubility of TlBr like that of PbI₂ and PbBr₂ is lower than that of "ordinary" TlBr; we have determined that the product [Tl⁺][Br⁻] for saturated TlBr in 1 M KNO₃ at 25° is 16.5×10^{-6}. We should emphasize that the Tl⁺ adsorption data represent equilibrium values; no increases in Γ_{Tl} result, on either plateau, from increasing the stirred equilibration of electrode with solution from 1 to 10 min.

K_{surp} for both discontinuities exhibit two further characteristics expected of equilibrium constants. (i) In 1 M KNO₃, K_{surp} increases with temperature. A plot of log K_{surp} *vs.* $1/T$ is linear, as expected for a solubility product. (ii) The value of K_{surp} is influenced by coordination of Tl⁺ by the supporting electrolyte anion in an entirely predictable manner. Thus, if [KNO₃] is lowered, or if KF electrolyte is employed, the apparent surface solubility of TlBr decreases. Application of the literature constants for complexation of Tl⁺ by NO₃⁻ or F⁻ quantitatively corrects for this effect as shown by comparison of K_{surp}' at each discontinuity for the three electrolyte solutions of Table I.