was then heated at 130° for 2 hr. The crude product was distilled from the reaction mixture in 90% yield using an aspirator. Distillation using a spinning band column gave a sample: bp 165° (740 mm); $n^{22}\mathrm{D}$ 1.4531 (lit.[48] bp 58–60° (15 mm), $n^{22}\mathrm{D}$ 1.4503).

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[48] H. B. Hass and H. C. Huffman, *J. Amer. Chem. Soc.*, **63**, 1233 (1941).

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The Thermal Decomposition of Substituted 1,2-Dioxetanes. A Consideration of Mechanism

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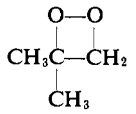
Abstract: Kinetic data for the thermal decomposition of the cyclic peroxides, 3,3-dimethyl-1,2-dioxetane (**1**) and 3-methyl-3-phenyl-1,2-dioxetane (**2**), in carbon tetrachloride solution are reported. First-order dependence is indicated and the observed activation parameters for **1** and **2** are: $E_a = 23.0 \pm 0.1$ kcal/mol, $\log A = 12.2$ and $E_a = 22.9 \pm 0.2$ kcal/mol, $\log A = 12.1$, respectively. The similarity of activation parameters for **1** and **2** is consistent with a two-step decomposition mechanism. Calculated activation parameters, based on this mechanism, are in reasonable agreement with the observed values. In further support of the two-step mechanism, the reported rate coefficients for alkoxy-substituted 1,2-dioxetanes can be estimated and also show good agreement with those observed. It appears that the previously calculated activation parameters for methyl-substituted 1,2-dioxetanes will serve to estimate kinetic data for diversely substituted 1,2-dioxetanes.

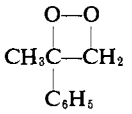
Thermal decomposition of 1,2-dioxetanes is a particularly fascinating reaction, since the ground-state cyclic peroxide produces a carbonyl-containing molecule in an excited singlet state.[1] Preliminary reports of this reaction to effect "photochemistry without light" have been made.[2] The reaction is also of importance to certain biological systems, where bioluminescence is thought to originate from the decomposition of 1,2-dioxetanes.[3]

We have reported some reactions of 1,2-dioxetanes,[4] but the simplest reaction, unimolecular thermal decomposition, is not well understood. Either a concerted process or a two-step mechanism may be operative. Calculations based on orbital symmetry considerations have been made for the concerted process by Kearns and coworkers[5] and we have made thermochemical kinetic[6] calculations based on the two-step mechanism.[7] We now report an experimental test of the two-step mechanism by a study of the thermal decomposition kinetics of 3,3-dimethyl-1,2-dioxetane (**1**) and 3-methyl-3-phenyl-1,2-dioxetane (**2**) in carbon tetrachloride. According to the two-step mechanism, resonance interactions by substituents are ruled out, while these effects could influence the rate of the concerted mechanism where π-carbonyl character may be developed in the activated complex.



$$\begin{array}{ll} & \mathrm{O{-}O} \\ & \mid\quad\;\mid \\ \mathrm{CH_3} & \mathrm{C{-}CH_2} \\ & \mid \\ & \mathrm{CH_3} \end{array}$$

1



$$\begin{array}{ll} & \mathrm{O{-}O} \\ & \mid\quad\;\mid \\ \mathrm{CH_3} & \mathrm{C{-}CH_2} \\ & \mid \\ & \mathrm{C_6H_5} \end{array}$$

2

Results

Preparation of 1,2-Dioxetanes. The preparation and characterization of **1** was reported previously.[4b] Treatment of 1-bromo-2-phenyl-2-hydroperoxypropane with methanolic base at 0° for a limited reaction period, followed by carbon tetrachloride extraction, gave **2** in 15% yield.[8] Unreacted hydroperoxide was removed by base extraction. The nmr spectrum showed the methyl and methylene protons to be in the correct ratio for **2**. A presumed contaminant, 1,2-dibromo-3-phenylpropane, which was believed to be formed in the preparation of the hydroperoxide, did not allow a comparison of the phenyl proton ratio. This contaminant remained unchanged throughout the decomposition of **2**. The concentration of **2** in the carbon tetrachloride solution was determined by nmr methods and checked iodometrically,[9] which indicates that the

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[1] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

[2] (a) E. H. White, J. Wiecko, and D. R. Roswell, *J. Amer. Chem. Soc.*, **91**, 5194 (1969); (b) E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970).

[3] *Cf.* W. D. McElroy, H. H. Seliger, and E. H. White, *Photochem. Photobiol.*, **10**, 153 (1969).

[4] (a) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 749 (1971); (b) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, **93**, 3996 (1971); (c) W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 1216 (1970); (d) W. H. Richardson and V. F. Hodge, *Tetrahedron Lett.*, 2271 (1970); (e) W. H. Richardson, J. W. Peters, and W. P. Konopka, *ibid.*, 5531 (1966).

[5] (a) D. R. Kearns and A. U. Khan, *Photochem. Photobiol.*, **10**, 193 (1969); (b) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

[6] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[7] H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970).

[8] The preparation of **2** was reported in a communication[2b] by a somewhat different method, but without experimental detail or physical properties.

[9] W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 247 (1965).

peroxidic compound was **2** and not unreacted bromo hydroperoxide.

Products. Previously we reported that the thermal decomposition of **1** in carbon tetrachloride produced a 90% yield of acetone as determined by glc analysis.[4b] The companion product, formaldehyde, was identified by its dimedon derivative in the basic decomposition of chloro-*tert*-butyl hydroperoxide in aqueous methanol.[4b] Thermal decomposition of **2** in carbon tetrachloride solution gave acetophenone in 97% yield as determined by nmr methods. Analysis by glc indicated a quantitative yield of the ketone. The stoichiometry of the reaction requires that formaldehyde must be the companion product, but a quantitative analysis for this product was not made. Mass spectral analysis of **2** did indicate that formaldehyde was formed from **2** along with acetophenone. The molecular ion of **2** was not observed and the mode of decomposition of **2** in the spectrometer is unknown.

Kinetics. Most of the kinetic data were obtained by nmr analyses. The rate of disappearance of **1** or **2** can be followed by observing either the methyl or methylene absorptions relative to an internal reference absorption. Benzene was used as the internal reference standard with **1** and the total aromatic absorption was used with **2**. Since changes in absorptions during the reaction are greatest for the methyl protons in **1** and **2**, these absorptions are normally used. To verify the nmr method, the rate of decomposition of **2** was checked by an iodometric method[9] (Table I). To establish first-order dependence in the 1,2-dioxetane, rate coefficients were determined for **2** over an initial tenfold concentration range (Table II). Data used to determine activation parameters for **1** and **2** are given in Table I and the resulting activation parameters are recorded in Table III.

Table I. Kinetic Data for the Thermal Decomposition of **1** and **2** in Carbon Tetrachloride at Various Temperatures[a]

1,2-Dioxetane	Temp, °C	10^4k,[b] sec^{-1}
1	39.66	1.18 ± 0.02
1	50.41	3.99 ± 0.11
1	54.61	6.40 ± 0.21
1	59.97	11.4 ± 0.2
1	70.03	31.3 ± 0.5
2	39.92	1.20 ± 0.03[c]
2	39.80	1.18 ± 0.02
2	50.02	3.99 ± 0.10
2	60.09	11.0 ± 0.2
2	69.84	30.6 ± 0.6

[a] Rates by nmr method unless specified otherwise. [b] First-order rate coefficients are determined by a least-squares program and they are given with probable error. [c] Rate by iodometric method.

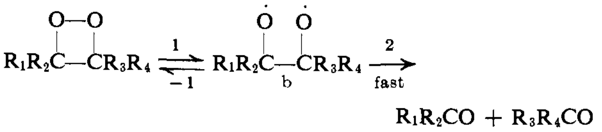
Table II. Effect of Initial Concentration on the Rate of Decomposition of **2** in Carbon Tetrachloride at 59.92° [a]

[2] × 10^2, *M*	10^3k,[b] sec^{-1}
3.51	1.10 ± 0.02
8.42	1.03 ± 0.01
17.6	1.03 ± 0.02
35.1	1.11 ± 0.01

[a] Rate data by nmr method. [b] Rate coefficients are determined by a least-squares first-order program and they are reported with probable error.

Discussion

As seen from Table II, the decomposition of **1** and **2** proceeds by a first-order process. Either a concerted mechanism or a two-step process (eq 1) can explain this observation. Our previous calculations, based on the two-step mechanism,[7] for methyl-substituted 1,2-dioxetanes are determined solely by steps 1 and −1 in eq 1. With this simplifying assumption, it is predicted that considerable liberties can be made in exchanging methyl for other substituents (R_1–R_4) without greatly affecting rates of decomposition. In contrast, if a concerted mechanism is operative, it might be expected that the exchange of R_1 = methyl for phenyl (*i.e.*, **1** *vs.* **2**) would cause a noticeable change in rate.



$$R_1R_2C(O\text{—}O)CR_3R_4 \underset{-1}{\overset{1}{\rightleftharpoons}} \underset{b}{R_1R_2\dot{O}C\text{—}C\dot{O}R_3R_4} \xrightarrow[\text{fast}]{2} R_1R_2CO + R_3R_4CO \quad (1)$$

This expectation is based on an analogy of the dissociation kinetics of alkyl-substituted cyclobutanes compared to acyl- and carboxyl-substituted cyclobutanes (Table IV). The data show that replacement of an alkyl substituent by an acyl or carboxyl group results in an activation energy decrease of about 8 ± 2 kcal/mol. The activation energy effects are clearly not caused by decreasing reaction exothermicities since these only change by ±2 kcal/mol. Alkyl-substituted cyclobutane reactions are classic examples of two-step consecutive processes which probably involve biradical intermediates. In order for the acyl- and carboxyl-substituted cyclobutanes to follow the same kind of "biradical mechanism," energy considerations require a carbonyl and carboxyl allylic-type resonance of about 8 kcal/mol.[10] However, recent measurements of the (C–H) bond dissociation energy in acetone do not show any appreciable carbonyl allylic-type resonance energy: $DH°(CH_3COCH_2H)$ = 98 ± 2 kcal/mol, which is the same (C–H) bond dissociation energy as found for ethane.[11,12] The acyl- and carboxyl-substituted cyclobutane decompositions are therefore not biradical processes and they are most readily explained by a concerted mechanism. Operationally, an appreciable rate acceleration is affected by these substituents.

Replacement of methyl in **1** by phenyl to give **2** places a π-electron substituent on the four-membered 1,2-dioxetane ring, much like the acyl and carboxyl substitutions in the cyclobutanes. In both the 1,2-dioxetane and cyclobutane systems with π-electron substituents, the decomposition products have a carbonyl group conjugated with a carbon–carbon π function. Based on this analogy between the two systems, one might expect that the π-electron substituent in **2** would accelerate reaction rates relative to those of the two-step biradical process thought to be operative with **1**. Considering the similarity of the rate data for **1** and **2** the qualitative interpretation must be that no such acceleration occurs. Rather, the data are consistent with the two-step process for both of the 1,2-dioxetanes.

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(10) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(11) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 11 (1970).

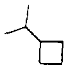
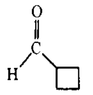
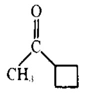
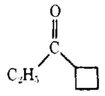
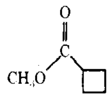
(12) K. D. King, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **92**, 5541 (1970).

Table III. Activation Parameters for the Decomposition of **1** and **2** in Carbon Tetrachloride[a]

1,2-Dioxetane	E_a[b]	Log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1	23.0 ± 0.1	12.2	22.4 ± 0.1	−5.0 ± 0.2
2	22.9 ± 0.2	12.1	22.3 ± 0.2	−5.3 ± 0.9

[a] From rate data *via* nmr method. Activation parameters are obtained by a least-squares program and they are given with probable error.

Table IV. Decomposition Kinetics of Some Substituted Cyclobutanes[a]

Reactant	Products	Log A[a]	E_a[b]	$\Delta H°_{\text{reaction}}$[b]	Ref[c]
	$C_3H_6 + C_2H_4$	15.38	61.2	18.0	*d*
	$CH_2{=}CHCH_2CH_2CH_3 + C_2H_4$	15.53	61.6	17.7	*e*
	$CH_2{=}CHCH(CH_3)_2 + C_2H_4$	15.63	62.6	16.7	*f*
	$CH_2{=}CHCH{=}O + C_2H_4$	14.43	53.3	15.5	*g*
	$CH_3COCH{=}CH_2 + C_2H_4$	14.53	54.5	14.8	*h*
	$C_2H_5COCH{=}CH_2 + C_2H_4$	14.51	54.2	14.9	*i*
	$CH_2{=}CHCOOCH_3 + C_2H_4$	14.83	57.3	16.2	*j*

[a] sec^{-1}. [b] kcal/mol. [c] Kinetic data all summarized and analyzed in: S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **21** (1970). [d] M. N. Das and W. D. Walters, *Z. Phys. Chem.* (*Frankfurt am Main*), **15**, 23 (1958). [e] S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961). [f] M. Zupan and W. D. Walters, *ibid.*, **67**, 1845 (1963). [g] B. C. Roquitte and W. D. Walters, *J. Amer. Chem. Soc.*, **84**, 4049 (1962). [h] L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958). [i] B. C. Roquitte and W. D. Walters, *J. Phys. Chem.*, **68**, 1606 (1964). [j] M. Zupan and W. D. Walters, *J. Amer. Chem. Soc.*, **86**, 173 (1964).

Table V. Thermochemical Parameters for Dioxetanes **1** and **2** and the Corresponding Biradicals **1b** and **2b**

Species	$S°$ (intrin)[a]	$\Delta S°_{1,-1}$[a]	$\Delta H_f°$[b]	$\Delta H°_{1,-1}$[b]	E(strain)[b]
1[c]	83.8	3.1	−18.3	14.4	26
1b[c]	86.9		−3.9		0
2	103.4	3.1	14.8	14.4	26
2b	106.5		29.2		0

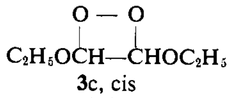
[a] eu. [b] kcal/mol. [c] Values previously reported in ref 7.

Table VI. Calculated Activation Parameters for the Thermal Decomposition of **1** and **2**

1,2-Dioxetane	E_a[a]	$\Delta S^{\ddagger}_{-1}$[b,d]	$\Delta S^{\ddagger}$[b]	Log A[c]	10^4k,[c] 60°
1[e]	22.9	−5.4	−2.3	12.9	72
2	22.9	−5.9	−2.8	12.65	44

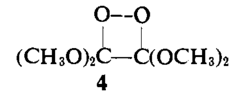
[a] kcal/mol, with E_{-1} = 8.5 kcal/mol. [b] eu. [c] sec^{-1}. [d] For methods of calculation see ref 10. [e] From ref 7.

Thermochemical kinetic calculations[6] for **1** and **2**, based on the two-step mechanism, support the observed similarity of kinetic parameters. The calculated thermochemical values for **1** and **2**, along with the corresponding biradicals **1b** and **2b**, are given in Table V. From the values in Table V, activation parameters may be calculated for the decomposition of 1,2-dioxetanes[7] and these values are given in Table VI. The calculated parameters for **1** and **2** are quite similar as expected. The agreement between calculated and observed activation energies is excellent for both **1** and **2**. There is fair agreement between calculated and observed log A values for **2** and the agreement would be improved if account was made for rotation barrier differences in **2** *vs.* **2b** for methyl and phenyl. This would lower the calculated log A value to 12.4 as compared to the observed value of 12.1. The poorest agreement between calculated and observed parameters is found with the log A values of **1**. A similar barrier correction for **1** would lower the calculated log A value to 12.7, but agreement with the observed value (12.2) is still poor. This parameter is of course most susceptible to error both in calculation and experimentally. The net effect is that the calculated rate coefficients are 6.3-fold and 4.0-fold greater than the observed values for **1** and **2** (*cf.* Tables II and VI), respectively, without barrier corrections. With these corrections the calculated rate coefficients are 4.0-fold and 2.3-fold greater for **1** and **2**. The agreement between calculated and observed rate coefficients for **2** is suitable to lend strong support to the two-step mechanism. Although the agreement is less than desired for **1**, it is not unreasonable considering the errors inherent in the log A parameter.



$$\overset{O-O}{C_2H_5OCH-CHOC_2H_5}$$

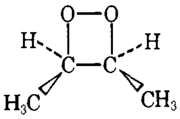
3c, cis
t, trans



$$\overset{O-O}{(CH_3O)_2C-C(OCH_3)_2}$$

4

Additional kinetic data were reported[13] recently for the decomposition of alkoxy-substituted 1,2-dioxetanes **3** and **4**, which provides another test of the two-step mechanism. Unfortunately, the $\Delta H_f°$ value for the $[\mathrm{C}(\dot{\mathrm{O}})(\mathrm{O})(\mathrm{C})(\mathrm{H})]$ group that is required to calculate the thermochemistry of the biradical from **3** is not available. Similarly, some group additivity values are lacking for thermochemical calculations involving **4**. Nonetheless, considerable liberties may be taken in the replacement of methyl for other groups in calculations based on the two-step decomposition of 1,2-dioxetanes as seen from **1** and **2**. A good estimate of the rate coefficients for **3c** and **4** can be made by using the calculated activation parameters for the corresponding methyl-substituted 1,2-dioxetanes[7] **5** and **6**. Thus, we estimate the rate coefficient for decomposition of **3c** to be 8×10^{-3} sec^{-1} at 54°, based on **5**, as compared to the reported value of 3.17×10^{-3} sec^{-1} at this temperature.[13a] With **6** as the model for **4**, we estimate the rate coefficient to be 8×10^{-5} sec^{-1} at 56° *vs.* a reported value of 12×10^{-5} sec^{-1} at the same temperature.[13b,14] The agreement is very good, particularly in view of equating methyl and alkoxy groups in the comparison.



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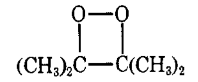
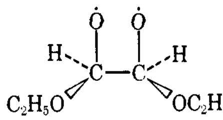


$$\overset{O-O}{(CH_3)_2C-C(CH_3)_2}$$

6

In summary, the two-step mechanism for the thermal decomposition of 1,2-dioxetanes can readily accommodate the existing kinetic data. Substituent effects are rationally explained by the thermochemistry of step (1, −1) of eq 1, but are not easily explained by a concerted process where substituents can interact with the developing carbonyl group. Admittedly, the argument against the concerted mechanism is qualitative, since a quantitative calculation based on this process is not possible by thermochemical methods. The two-step mechanism does appear most reasonable at this time and it has the practical advantage of giving reasonable estimates of activation parameters. In fact, the calculated parameters for the various methyl-substituted 1,2-dioxetanes[7] appear to serve as reasonable estimates for other substituted 1,2-dioxetanes, where the type of substituent varies widely.

As a by-product, the success of the estimate of the rate coefficient for **3c**, based on **5**, allows the estimation of $\Delta H_f°$ for a new group. The heat of formation of **3c** ($\Delta H_{f_{3c}}°$) is calculated to be −99.6 kcal/mol and $\Delta H_{f_7}° - \Delta H_{f_{3c}}° = 13.2$ kcal/mol, based on **5**.[7] The additivity values for all groups comprising $\Delta H_{f_7}°$ are known, except for $[\mathrm{C}(\mathrm{O}\cdot)(\mathrm{O})(\mathrm{C})(\mathrm{H})]$, which is then calculated to be −2.4 kcal/mol. This predicts a value for the OH bond dissociation energy in compounds like (ROCHROH) of $DH°(\mathrm{R'OH}) \simeq 104.8$ kcal/mol, which is reasonable[15] and supports the $\Delta H_f°$ value for $[\mathrm{C}(\mathrm{O}\cdot)(\mathrm{O})(\mathrm{C})(\mathrm{H})]$.



7

Experimental Section[16]

1-Bromo-2-phenyl-2-hydroperoxypropane. The general method of preparation was similar to that reported previously for other bromo hydroperoxides.[17] To a stirred solution of 4.72 g (40.0 mmol) of freshly distilled α-methylstyrene (Matheson Coleman and Bell (MCB)) in 100 ml of anhydrous ether at −40° was added 6.8 g (200 mmol) of 98% hydrogen peroxide (FMC) with stirring and then 5.72 g (20.0 mmol) of 1,3-dibromo-5,5-dimethylhydantoin (MCB, 98% pure by iodometric titration[9]) in portions over a 10-min period. The reaction mixture was protected by a nitrogen atmosphere. After the addition was completed, the reaction mixture was allowed to come to room temperature over a 60-min period. The colorless solution was washed repeatedly with a cold saturated sodium bicarbonate solution and then with cold water. The ether extract was dried over anhydrous magnesium sulfate and then concentrated on a rotary evaporator to give 8.18 g of a colorless, viscous liquid, which was 78.5% pure hydroperoxide by iodometric titration[9] (69.5% yield): nmr (CCl_4) CH_3 (1.65, s, 2.9), CH_2Br (3.77, s, 2.0), OOH and C_6H_5 (7.33, multiplet, 5.9); (dimethyl sulfoxide (DMSO)) OOH (11.32, s, 1.0) and C_6H_5 (7.33, multiplet, 5.6). From the OOH chemical shift in DMSO, the pK_a of the hydroperoxide is calculated to be 13.0,[18] which agrees well with the calculated pK_a of 12.9 based on σ^* values.[18]

3-Methyl-3-phenyl-1,2-dioxetene (2). To 2.00 g of 78.5% pure (6.80 mmol) 1-bromo-2-phenyl-2-hydroperoxypropane in 14 ml of methanol at 0° was added a solution of 0.40 g (10 mmol) of sodium hydroxide and 0.5 ml of water in 20 ml of methanol over a 10-min period with stirring. Stirring was continued for an additional 40 min at 0° and then 14 ml of cold water was added dropwise. The solution was rapidly extracted with carbon tetrachloride and the organic extract was repeatedly washed with a cold 1 *M* sodium hydroxide solution and then with cold water. The carbon tetrachloride solution was stored over anhydrous sodium sulfate in a freezer (*ca.* −20°). Based on the nmr signal of the methyl protons of **2** relative to a solution of ethyl acetate of known concentration, the concentration of **2** was 4.29×10^{-3} *M*. Iodometric titration of the solution gave a value of 4.15×10^{-3} *M*, which corresponds to a 15.4% yield of **2**. The nmr of **2** showed: (CCl_4) (external TMS) CH_3 (1.83, s, 3.0), CH_2 (5.00, s, 2.0), and C_6H_5 (7.1, multiplet, 13.8); (perdeuterioacetone) CH_3 (1.97, s, 2.9) and CH_2 (5.28, 5.30, 2.0). The large aromatic absorption was believed to be due to contamination by 1,2-dibromo-2-phenylpropane. Carbon tetrachloride was selectively distilled from a solution of **2** in this solvent at 10 mm with the pot at room temperature to give a viscous oil. A mass spectrum of the oil was measured with the spectrometer reservoir at room temperature and ionization voltages ranging from 4 to 80 V. The molecular ion of **2** was not observed, but instead ions associated with acetophenone (*m/e* 120 (M^+), 105 ($C_6H_5CO^+$), and 77 ($C_6H_5^+$)) and formaldehyde (*m/e* 30 (M^+) and 29 (CHO^+)). The nmr spectrum of the sample was void of acetophenone, before the mass spectral analysis.

Products from 2. A 4.61×10^{-2} *M* carbon tetrachloride solution of **2** was heated in a sealed nmr tube for 23 hr at 40°. At this time, the nmr signals for **2** were no longer present and the methyl resonance for acetophenone (2.48, s) appeared. A 97% yield of acetophenone was calculated from the nmr spectrum relative to a

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[13] (a) P. D. Bartlett and A. P. Schaap, *J. Amer. Chem. Soc.*, **92**, 3223 (1970); (b) S. Mazur and C. S. Foote, *ibid.*, **92**, 3225 (1970).

[14] A first-order rate coefficient of 12×10^{-5} sec^{-1} is calculated from the reported[13b] half-life of 102 min at 56°.

[15] $DH°(CH_3OH) = 103.6$ kcal/mol: S. W. Benson and R. Shaw, *Advan. Chem. Ser.*, No. **75**, 288 (1968).

[16] Temperatures of kinetic measurements are corrected. The nmr spectra were measured in carbon tetrachloride solution, unless specified otherwise, with a Varian A-60 spectrometer. Tetramethylsilane is the internal standard, except in kinetic measurements, and the data are reported on the δ scale in parts per million (δ, coupling, area). Mass spectral analysis was obtained with a Hitachi RMU-6E spectrometer. Glc analyses were performed with a Varian-Aerograph Hy-FI-III, flame ionization instrument.

[17] K. R. Kopecky, J. H. van de Sande, and C. Mumford, *Can. J. Chem.*, **46**, 25 (1968).

[18] W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 4012 (1970).

solution of ethyl acetate of known concentration. Analysis by glc (5 ft × 1/8 in. 3% SE-30 on Variport column, 80°, flow 25 ml/min of nitrogen), relative to a biphenyl internal standard and a standard mixture of acetophenone and biphenyl in carbon tetrachloride solution, indicated a quantitative yield of acetophenone.

Kinetic Methods. Iodometrically determined rates were made by a standard procedure.[9] For nmr data, the reactions were carried out in sealed nmr tubes. The tubes were periodically withdrawn from a constant temperature oil bath and quenched in a −78° bath. After warming to room temperature, the nmr spectrum was immediately measured and the 1,2-dioxetane methyl and methylene as well as reference absorptions were integrated. The rate of decomposition of the 1,2-dioxetanes was slow enough at room temperature that essentially no decomposition occurred during the measurements. For **1**, benzene was added to the solution as an internal reference and the total aromatic absorption was used as the reference for **2**. Area ratios of the methyl 1,2-dioxetane to reference absorptions were normally used to calculate the rate coefficients with the aid of a standard least-squares first-order computer program. The methylene absorptions of the 1,2-dioxetanes gave essentially the same rate coefficients, but usually with less precision.

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On the Kinetics and Mechanism of the Perkow Reaction[1]

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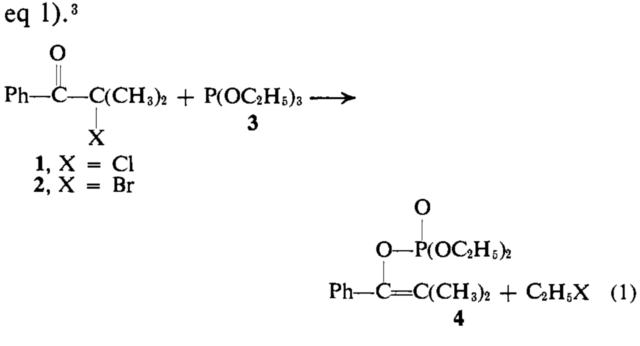
Abstract: The reactions of aryl-substituted α-chloroisobutyrophenones and α-bromoisobutyrophenones with triethyl phosphite to give diethyl 1-phenyl-2,2-dimethylvinyl phosphate (the Perkow reaction) have been studied kinetically by an nmr technique. The reactions are second order overall and they exhibit a moderate solvent effect. The chloro ketones react 1.1–2.7 times faster than the corresponding α-bromo ketones. ρ values for the two series are 1.89 and 2.37, respectively. The reaction of α-chloroisobutyrophenone with triethyl phosphite exhibits a marked catalysis by added acetic acid which is proportional to the concentration of acid. This and other accumulated data support a mechanism for the Perkow reaction involving a rate-determining addition of phosphite to carbonyl carbon followed by rearrangement of the phosphorus to oxygen. The stereochemistry of the carbonyl addition is proposed as occurring mainly from the less hindered side of the halogen eclipsed or gauche forms of the α-halo ketone. This is a rationalization of our recent findings that the vinyl phosphate E isomer is more predominantly formed from bromo ketones than from chloro ketones.

The Perkow reaction is exemplified by the reaction of α-chloroisobutyrophenone (**1**) or α-bromoisobutyrophenone (**2**) with triethyl phosphite (TEP, **3**) to give diethyl 1-phenyl-2,2-dimethylvinyl phosphate (**4**, eq 1).[3]



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle X}{|}}{C}(CH_3)_2} + \underset{\mathbf{3}}{\mathrm{P(OC_2H_5)_3}} \longrightarrow \underset{\mathbf{4}}{\mathrm{Ph{-}\overset{\overset{\displaystyle O{-}\overset{\overset{\displaystyle O}{|}}{P}(OC_2H_5)_2}{|}}{C}{=}C(CH_3)_2}} + \mathrm{C_2H_5X} \quad (1)$$

1, X = Cl
2, X = Br

Although numerous studies have appeared on the scope and mechanism of the Perkow reaction,[3,4] no kinetic studies have been reported. We wish to report a kinetic study on the reactions of a series of aryl-substituted α-chloroisobutyrophenones and α-bromoisobutyrophenones with triethyl phosphite wherein rates, activation parameters, Hammett ρ values, and the effect upon rates of solvent and added acetic acid have been determined. Some new nonkinetic data will also be presented. A suggested mechanism based on the accumulated data will be presented and discussed. Our recent finding that the E isomeric vinyl phosphate usually predominates will be rationalized.

Results

The reaction of **1** or **2** with **3** was studied in benzene using an nmr technique (see Experimental Section). The reactions are first order in halo ketone and first order in **3**, as shown by linear plots of $x/(a - x)$ *vs.* time. The relative constancy of k_{obsd} for the reaction of **2** with **3** for differing ratios of reactants is shown in Table I.

The reactions give the vinyl phosphate **4** as the only product. The rates and relative rates of reaction of aryl-substituted **2** with **3** at 44.9° are given in Table II.

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[3] I. J. Borowitz, M. Anschel, and S. Firstenberg, *J. Org. Chem.*, **32**, 1723 (1967).

[4] (a) F. W. Lichtenthaler, *Chem. Rev.*, **61**, 607 (1961); (b) P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, *Tetrahedron*, 21, 1961 (1965). (c) Note Added in Proof. See A. Arcoria and S. Fisichella, *Tetrahedron Lett.*, 3347 (1971), for kinetics of diethyl 1-phenylvinyl phosphate formation.

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