mL of dry *n*-pentane–diethyl ether (3:2 by volume) containing 2.0 mmol of *n*-heptane as internal standard was cooled to −23 °C under a blanket of argon and 4.0 mmol of *t*-BuLi as a solution in pentane was added via syringe over a 5-min period. The reaction mixture was stirred for 30 min −23 °C, the cooling bath was removed, and 10 mL of water was cautiously added. After warming to room temperature, the organic phase was separated, dried ($MgSO_4$), and analyzed by GLC on column A at 35 °C. The results are presented in Scheme II. Methylcyclopentane and 1-hexene were identified by comparison of their retention times and mass spectra obtained by GC/MS with those of authentic samples.

Acknowledgment. This investigation was supported by a grant from the Humphrey Chemical Company, North Haven, CT, and we are grateful for their continued interest in our work. We acknowledge with thanks the help of Marvin Thompson in obtaining numerous high-resolution mass spectra. WFB thanks Professor Jack Baldwin of the Dyson Perrins Laboratory, Oxford, for his kind hospitality during the period when this paper was written.

Registry No. 3, 85807-81-4; 4, 89891-12-3; 5, 37746-17-1; 6, 2695-47-8; 7, 18922-04-8; *t*-BuLi, 594-19-4; $I(CH_2)_5I$, 628-77-3; $I(CH_2)_5Br$, 88962-86-1; $I(CH_2)_5Cl$, 60274-60-4; $I(CH_2)_6I$, 629-09-4; *n*-C_6H_{14}, 110-54-3; *n*-$C_{12}H_{26}$, 112-40-3; *n*-$C_{18}H_{38}$, 593-45-3; *n*-C_7H_{16}, 142-82-5; *n*-$C_{14}H_{30}$, 629-59-4; 1,3-diiodo-2,2-diethylpropane, 85807-77-8; 1,4-diiodo-2-phenylbutane, 85807-78-9; *cis*-1,2-bis(2-iodoethyl)cyclohexane, 85807-79-0; *exo,cis*-1,2-bis(iodomethyl)-bicyclo[2.2.1]heptane, 85807-80-3; *cis*-1,2-bis(iodomethyl)cyclobutane, 77774-05-1; *cis*-1,2-bis(2-iodoethyl)cyclohexane, 85807-82-5; 1,7-diiodoheptane, 51526-03-5; 1,1-diethylcyclopropane, 1003-19-6; phenylcyclobutane, 4392-30-7; *cis*-bicyclo[4.2.0]octane, 28282-35-1; *exo,cis*-tricyclo[4.2.1.$0^{2,5}$]nonane, 16526-27-5; cyclopentane, 287-92-3; 1,1-dimethylcyclopentane, 1638-26-2; 1,5-hexadiene, 592-42-7; cyclohexane, 110-82-7; *tert*-butylcyclohexane, 3178-22-1; *cis*-decahydronaphthalene, 493-01-6; cycloheptane, 291-64-5; 3,3-dimethylpentane, 562-49-2; 2,2,5,5-tetramethylheptane, 61868-47-1; 2,2,5,5,8,8-hexamethylnonane, 89891-14-5; 3,3,8,8-tetramethyldecane, 85807-83-6; 2,2,5,5,10,10-hexamethyldodecane, 89891-15-6; methylcyclopentane, 96-37-7; 1-hexene, 592-41-6; 2,2-diethyl-1,3-propanediol, 115-76-4; *cis*-1,2-bis(2-hydroxyethyl)cyclohexane, 59434-70-7; *cis*-1,2-bis(hydroxymethyl)cyclobutane, 54445-64-6; 2-phenyl-1,4-butanediol, 6837-05-4; 3,3-dimethyl-1,5-pentanediol ditosylate, 53120-76-6; 5-bromo-1-pentene, 1119-51-3; 3-*tert*-butyl-1,6-hexanediol, 82111-97-5; 4-*tert*-butylcyclohexene, 2228-98-0; 3-*tert*-butyl-1,6-hexanediol ditosylate, 89891-16-7; 5-hexene-1-ol mesylate, 64818-36-6; 3-*tert*-butyl-1,6-diiodohexane, 89891-13-4.

Kinetics and Mechanism of Acetone Cyclic Diperoxide (3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane) Thermal Decomposition in Benzene Solution

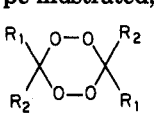
L. F. R. Cafferata,* G. N. Eyler, and M. V. Mirífico

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Inifta, Casilla de Correo 16, Sucursal 4, 1900 La Plata, Argentina

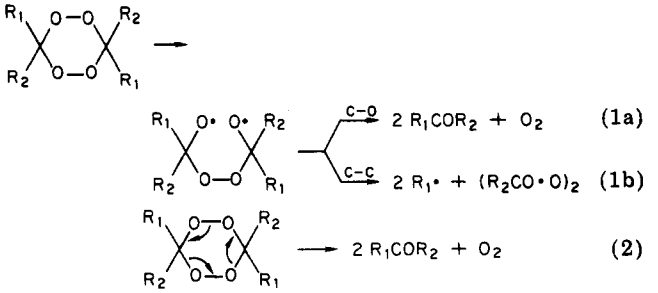
Received July 19, 1983

In the temperature range of 135.5 to 165.0 °C the main products of acetone cyclic diperoxide (ACDP) thermolysis in benzene solution are oxygen, acetone, and toluene, with minor yields of methyl isopropyl ether, methyl acetate, bibenzyl, methyl alcohol, methane, ethane, and carbon dioxide. The overall reaction follows a first-order kinetic law up to 60% ACDP conversion. At temperatures ranging between 135.5 and 145.0 °C the observed rate constant values are independent of the initial ACDP concentration, but at 150.5 and 165.0 °C, with concentrations higher than 0.1 and 0.06 mol kg^{-1}, respectively, a nearly linear dependence between the rate constant and concentration can be established. The activation parameters for the ACDP unimolecular decomposition reaction are $\Delta H^{\ddagger}$ = 35.7 ± 1.1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = 0.0 ± 0.3 eu. Support for a stepwise mechanism instead of a concerted process is given by comparison of these parameters with those corresponding to alkyl peroxides and with the theoretically calculated activation energy for the ACDP homolysis. It is concluded that an induced decomposition of ACDP molecules by methyl radicals must be postulated in the thermolysis mechanism. That process, which gives oxygen, acetone, and methyl isopropyl ether as its products, has an estimated overall activation energy of 10 kcal mol^{-1}. In toluene solution at 165.0 °C this reaction is suppressed at ACDP initial concentration lower than 0.1 mol kg^{-1}.

It has been reported[1] that the thermal decomposition of diperoxides of the type illustrated, where R_1 and R_2 can



be the same or different groups (Me, Et, *t*-Bu, $-(CH_2)_5-$, Ph, and $PhCH_2$), give different products with yields dependent on the characteristics of the respective molecule substituents. For the decomposition of those peroxides, two main types of processes have been suggested: a stepwise mechanism with a biradical as intermediate, which further decomposes by C–O or C–C ruptures (Eq 1) and a concerted type decomposition (eq 2). The few



kinetic data for their reactions[2] and the scarce product

(1) (a) Mc Cullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L.; White, G. J. *J. Chem. Res. Synop.* **1980**, *34* M 0601. (b) Mc Cullough, K. J.; Morgan, A. R.; Nonhebel, D. C.; Pauson, P. L. *Ibid.* **1981**, *35*, M 0629; **1982**, *36*, M 0651.

0022-3263/84/1949-2107$01.50/0

Table I. Rate Constant Values for ACDP Thermal Decomposition

solvent	temp, °C	$10^3[ACDP]_0$[a]	10^6k_{exp}, s^{-1}	10^6k_0,[b] s^{-1}
benzene	135.5	50.0	0.615	
		110	0.631	
		230	0.630	0.625 ± 0.009
	140.5	50.0	1.24	
		100	1.23	
		249	1.11	1.19 ± 0.07
	145.5	53.0	2.08	
		125	2.13	
		127	2.06	
		185	2.09	2.09 ± 0.03
		53.0[c]	2.41	
		185[d]	2.75	
	150.5	16.9	2.91	
		21.9	2.85	
		44.5	2.71	
		51.5	2.80	
		100	2.89	2.83 ± 0.08
		140	3.13	
		211	4.15	
		223	4.37	
		232	4.43	
		323	4.82	
		78.1[e]	4.39	
		77.9[f]	4.56	
		77.3[g]	7.46	
		128[h]	7.42	
		134[i]	4.46	
		195[j]	5.01	
	165.0	20.0	14.2	
		53.0	14.2	
		60.0	13.9	14.1 ± 0.2
		101	15.4	
		110	15.6	
		153	16.8	
		230	18.9	
toluene	165.0	20.6	13.7	
		91.1	13.7	13.7 ± 0.0
		121	14.3	
		316	18.8	

[a] mol kg^{-1}. [b] Averages of the experimental rate constant values (k_{exp}) when they are practically independent of ACDP initial concentration; errors calculated as standard deviations. [c] STY added, 0.26 mol kg^{-1}. [d] STY added, 0.54 mol kg^{-1}. [e] AP added, 0.05 mol kg^{-1}. [f] AP added, 0.08 mol kg^{-1}. [g] AP added, 0.15 mol kg^{-1}. [h] DBC added, 0.4 mol kg^{-1}. [i] STY added, 0.5 mol kg^{-1}. [j] STY added, 0.7 mol kg^{-1} (see text).

analyses reported in the literature[1] do not support sufficiently the mechanism postulated.

In this work, the kinetics of acetone cyclic diperoxide ($R_1 = R_2 = Me$, ACDP) thermal decomposition in benzene solution have been studied. Other substances have been added, and the corresponding product analyses were simultaneously performed to learn about the reaction mechanism.

Results and Discussion

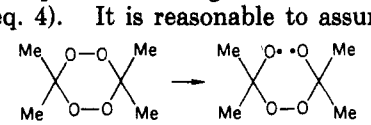
The thermal decomposition of ACDP in benzene and toluene solutions in the temperature and initial concentration ranges of 135.5 to 165.0 °C and (16.9–323) × 10^{-3} mol kg^{-1}, respectively, follows a first order law up to 60% diperoxide conversion. At the lower temperatures (135.5 to 145.0 °C) (Figure 1) the observed rate constant values are practically independent of the initial ACDP concentration, but at 150.5 and 165.0 °C, for concentrations higher than 0.1 and 0.06 mol kg^{-1}, respectively, an almost linear dependence is found. This behavior may be interpreted by postulating in the diperoxide reaction mechanism an induced decomposition of the ACDP molecule, because that kind of process usually causes an increase in rate with an increase in the initial concentration.

The temperature effect on the rate constant values, obtained when they are independent of ACDP initial concentration (k_0, Table I), can be represented by the Arrhenius eq 3 where the errors shown are standard de-

$$\ln k_0\ (s^{-1}) = (30.8 \pm 2.6) - (36{,}600 \pm 1{,}100)/RT \quad (3)$$

viations from a least mean square treatment[3] of the results.

The activation enthalpy value corresponding to eq 3, $\Delta H^{\ddagger} = 35.7 \pm 1.1$ kcal mol^{-1}, is similar to those reported for the homolytic unimolecular decompositions in solution of several dialkyl peroxides.[4] This suggests that the rate-determining step in the ACDP thermolysis is the rupture of one peroxidic linkage of its molecule, giving a biradical (eq. 4). It is reasonable to assume that the



(4)

biradical recombination[5] to rebuild the peroxide molecule is a fast, non-rate-determining process, in the proposed mechanism. The corresponding activation entropy value $\Delta S^{\ddagger} = 0.0 \pm 0.3$ eu differs from the values for most dialkyl

(2) (a) Sanderson, J. R.; Story, P. R. *J. Org. Chem.* **1974**, *39* (21), 3183. (b) Sanderson, J. R.; Paul, K.; Story, P. R.; Denson, D. D.; Afford, J. A. *Synthesis* **1975**, 159.

(3) Green, J. R.; Margerison, D. "Statistical Treatment of Experimental Data"; Elsevier: Amsterdam, 1978.

(4) Cafferata, L. R. F.; Quintáns, M. T. *Anales Asoc. Quím. Argentina* **1980** *68*, 129.

(5) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968; p 69.

Table II. Product Molar Yields (Moles of Product Per Mole of ACDP Decomposed) of ACDP Thermolysis (30% Conversion) in Different Conditions

solvent	temp, °C	$10^3[ACDP]_0$[a]	acetone	toluene	other compd
benzene	135.5 to 165.0	16.9 to 323	1.3 ± 0.2	0.6 ± 0.1	methyl acetate (~0.04), methyl isopropyl ether[b] (0.12 ± 0.01), methanol (~0.05), biphenyl (~0.06), bibenzyl, methane, ethane, oxygen, and carbon dioxide
benzene (+STY, 0.5 mol kg^{-1})	150.5	185	1.3 ± 0.2	0.06 ± 0.01	
benzene (+AP, 0.05 mol kg^{-1})	150.5	78.1	1.3	1.4	methyl acetate (0.12)
benzene (+AP, 0.08 mol kg^{-1})	150.5	77.9	1.2	1.4	methyl acetate (0.17)
benzene (+AP, 0.15 mol kg^{-1})	150.5	77.3	1.3	1.4	methyl acetate (0.27)
benzene (+AP, 0.094 mol kg^{-1})	150.5		5.10^{-3} [c]	0.2[c]	methyl acetate (0.12)[c]
toluene	165.0	20.6 to 316	1.2 ± 0.2		methyl acetate (~0.04), methanol, bibenzyl, benzaldehyde, and benzyl alcohol

[a] mol kg^{-1}. [b] Product found only when the induced decomposition is taking place. [c] Moles of product per mole of AP decomposed.

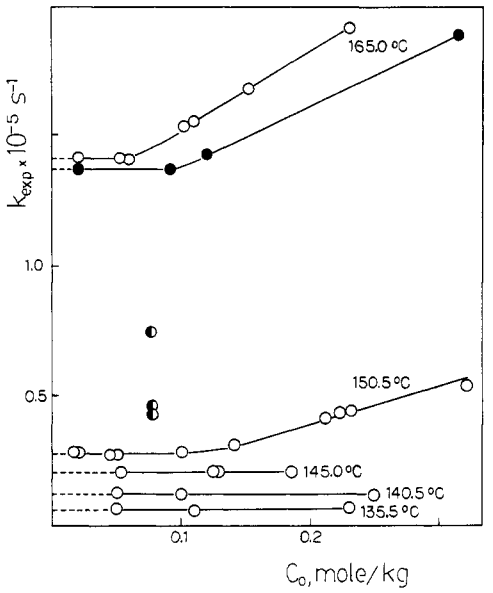


Figure 1. Rate constant values (k_{exp}) dependence with the ACDP initial concentration, at different temperatures (○, benzene solution; ◐, benzene with added AP at 150.5 °C; ●, toluene solution).

peroxides in solution (e.g., $\Delta S^{\ddagger}_{DTBP}$ = 9 eu[4]). For di-*tert*-butyl peroxide (DTBP) unimolecular homolysis that parameter is large and positive because two fragments are forming at the corresponding transition state. No such separation occurs in the substituted tetraoxane ring opening process and therefore the two reactions are not at all analogous. Then, the previously stated rate constant k_0 can be associated with the homolytic cleavage (k_1) of one peroxidic bond of the ACDP molecule (eq 4).

The Arrhenius equation plot for k_1 is linear (r = 0.996) in a relatively large temperature range (ca. 30 °C), which suggests that the above indicated activation parameters belong to a single process (eq 4). It is not probable that both the unimolecular homolytic reaction and the suggested[1] concerted process

$$ACDP \rightarrow 2\ Me_2CO + O_2 \qquad (5)$$

have identical activation parameters. A theoretical MNDO calculation with the half electron model for the triplet state,[6] with geometry optimization and double precision by the DFP method[7] was applied to the ACDP molecule rupture, with a zero barrier energy for the biradical recyclization; the resulting activation energy (E_1) was found to be 38.3 kcal mol^{-1}. This theoretical value, comparable to the experimentally obtained one in this work, corroborates the preceding postulate as to the rate-determining step of the ACDP thermolysis. Moreover, if the diperoxide thermolysis were of the concerted type, where the bond breaking at the transition state is partly compensated by bond making, the experimentally found activation energy would have been less than the theoretically calculated value and the corresponding activation entropy, with its highly ordered transition state, would turn to a very negative value.[8]

The kinetics of ACDP thermal decomposition in benzene solution with some conventional[9] free radical scavengers added (styrene (STY), 2,6-di-*tert*-butyl-*p*-cresol (DBC), see Table I) shows that the proposed induced reaction is not suppressed by those substances; instead, the corresponding overall decomposition rate constant value (k_{exp}) is increased, probably due to formation of reactive free radicals that attack the ACDP molecule more effectively than those produced in the thermolysis without those scavenger additions.

The k_0 value obtained in toluene solution (Figure 1) is coincident, within the experimental error, with the one corresponding to the benzene reaction at 165.0 °C, but the respective k_{exp} values show a larger range where they are independent of the initial ACDP concentration (Table I). These results indicate that the above mentioned induced decomposition is totally suppresed at the lower ACDP initial concentrations and only partially inhibited at the higher concentrations.

The addition to the benzene solution at 150.5 °C of acetyl peroxide (AP), a proved source of free methyl radical (which is also a suggested[1] intermediate in the ACDP decomposition mechanism) (Figure 1), increases the k_{exp} values directly and proportionally to the AP initial concentrations (Table I). Thus, it can be concluded that in the ACDP induced decomposition reaction the methyl

(6) Dewar, M. J. S.; Hashmall, J. A.; Verner, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953.

(7) (a) Fletcher, R.; Powell, M. J. D. *Comput. J.* **1963**, *6*, 163. (b) Davidon, W. C. *Ibid.* **1968**, *10*, 406.

(8) Jones, R. A. Y. "Physical and Mechanistic Organic Chemistry"; Cambridge University Press: Cambridge, 1979.

(9) (a) Richardson, W. H.; Mc Ginness, R.; O'Neal, E. *J. Org. Chem.* **1981**, *46* (9), 1887. (b) Koenig, T. In "Free Radicals"; Wiley: New York, 1973; Vol. I, Chapter 3. (c) Howard, J. A. In "Free Radicals"; Wiley: New York, 1973; Vol. II, Chapter 12.

Table III. Methyl Acetate Produced in the ACDP-Benzene-AP and Benzene-AP Systems at 150.0 °C

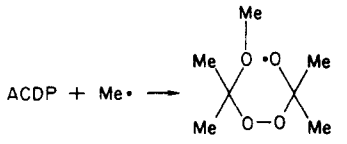
$10^3[ACDP]_0$, mol kg^{-1}	$[AP]_0$, mol kg^{-1}	10^3 mol methyl acetate[a] (ACDP-Bz-AP)	10^3 mol methyl acetate[a] (Bz-AP)	$10^3\Delta$[b]	methyl acetate,[c] molar yields
78.1	0.05	9	6	3	0.038
77.9	0.08	13	10	3	0.039
77.3	0.15	21	18	3	0.039

[a] In runs with total conversion of ACDP and AP. [b] Represents the methyl acetate arising from that AP resulting from ACDP thermolysis. [c] Coming from ACDP-benzene decomposition.

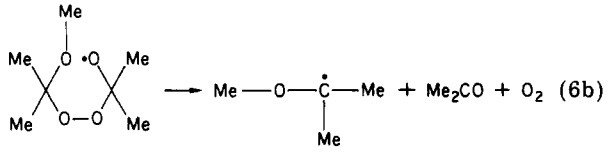
radicals are active participants. Because methyl isopropyl ether is a product only found when the induced decomposition is taking place (Table II), eq 6 may be postulated to interpret that reaction. This process probably occurs

$$ACDP + Me\cdot \xrightarrow[(-R\cdot)]{RH} Me_2CHOMe + Me_2CO + O_2 \quad (6)$$

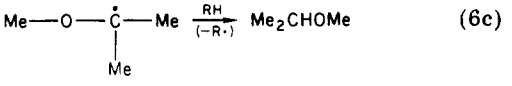
through the steps illustrated in eq 6a–6c.



(6a)



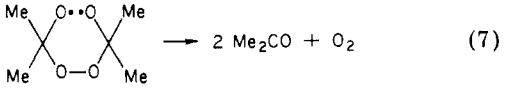
(6b)



(6c)

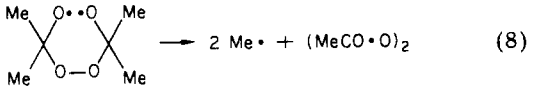
The main products of the ACDP thermolysis in benzene solution, coming from experiments performed in different conditions, are oxygen, acetone, and toluene with minor yields of methyl isopropyl ether, methyl acetate, biphenyl, bibenzyl, methyl alcohol, methane, ethane, and carbon dioxide (Table II).

Oxygen and acetone come from the fragmentation of the initially formed biradical (eq 4), through the rupture of their C–O linkages (eq 7) and also as products of the induced reaction (eq 6).



(7)

Methane and ethane result from hydrogen abstraction and combination reactions, respectively, of the methyl radicals produced in the biradical fragmentation through their C–C linkages breakdown (eq 8) and from the intermediate AP formed in the previous process (eq 9 and 10).



(8)

$$(MeCO\cdot O)_2 \rightarrow 2\ MeCO\cdot O\cdot \quad (9)$$

$$MeCO\cdot O\cdot \rightarrow Me\cdot + CO_2 \quad (10)$$

The observed methane:ethane ratio value is less than unity (0.2 in the liquid and 0.6 in the gaseous phase of the ampoules' contents), a result which shows that the methyl radical recombination predominates over the hydrogen abstraction reactions, excluding a predominant attack by methyl radicals on the alkyl groups of the ACDP molecule.

Methyl acetate formed in the presence of ACDP might be interpreted by an induced process (eq 11). However,

$$ACDP \xrightarrow{Me\cdot} 2\ MeCO\cdot OMe \quad (11)$$

methyl acetate obtained in benzene and toluene solutions arises only from the AP decomposition[10,11] (a finding that has been experimentally corroborated by a blank experiment, Table II) by coupling of the acetoxy and methyl radicals within the solvent cage.[12] In fact, the methyl acetate molar yields calculated taking the differences between the corresponding amounts of that substance obtained in the ACDP–benzene–AP and benzene–AP systems (see Table III) are practically coincident with the values observed in the ACDP–benzene and –toluene solutions (Table II). These results invalidate the above postulation (eq 11).

The acetone molar yield (Table II), similar to the value reported at 150.0 °C by other authors,[1] slowly decreases as the ACDP decomposition is taking place. This behavior can be explained by hydrogen atom abstraction[13] by methyl radicals (eq 12).

$$Me\cdot + Me_2CO \rightarrow MeH + \cdot CH_2C(=O)CH_3 \quad (12)$$

Under experimental conditions where the ACDP induced decomposition is unimportant, approximately 65% of the diperoxide disappears through the reactions represented by eq 4 and 7; instead, when the induced process contributes significantly to the overall reaction, the acetone yield should be 1.15 according to the proposed mechanism. The difference that should be observed (0.15 molar yield) between the two limiting conditions cannot be detected because of the analytical method employed in most of the GC analyses performed (the acetone retention time was about the same as the one corresponding to the methyl isopropyl ether).

The formation of toluene can be explained through the reactions of the methyl radicals with the benzene solvent (eq 13).

$$Me\cdot + PhH \rightarrow (C_6H_6Me)\cdot \xrightarrow[(-RH)]{(R\cdot)} PhMe \quad (13)$$

With added styrene, the toluene molar yield (Table II) is lower than the value obtained in pure benzene. This result corroborates the important participation of methyl radicals in the thermolysis. Furthermore, for the benzene reaction with an ACDP conversion higher than 30%, the toluene yield decreases and the bibenzyl yield increases as the reaction is completed. This can be interpreted with eq 14 and 15.

$$PhCH_3 \xrightarrow[(-RH)]{R\cdot} PhCH_2\cdot \quad (14)$$

$$2\ PhCH_2\cdot \rightarrow (PhCH_2)_2 \quad (15)$$

The remaining products of the ACDP thermolysis (Table II) can be explained by eq 16 and 17.

(10) Walling, Ch. "Free Radicals in Solution"; Wiley: New York, 1957.
(11) Pryor, W. A. "Free Radicals"; Mc Graw-Hill: New York, 1966.
(12) Nonhebel, D. C.; Walton, J. C. "Free-radical Chemistry"; Cambridge University Press: London, 1974; Chapter 1.
(13) Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Hydrogen Transfer Reactions of Methyl Radicals"; Butterworths: London and Boston, 1976.

$$Me\cdot + PhH \rightarrow MeH + Ph\cdot \quad (16)$$

$$Ph\cdot + PhH \rightarrow (PhC_6H_6)\cdot \xrightarrow[(-RH)]{R\cdot} PhPh \quad (17)$$

The overall rate constant value of the induced reaction (k_6) can be estimated considering the yields of toluene (eq 13) and methyl isopropyl ether (eq 6), using eq 18.

$$\frac{\text{methyl isopropyl ether yield}}{\text{toluene yield}} = \frac{k_6[\text{ACDP}]}{k_{13}[\text{benzene}]} \quad (18)$$

If the k_{13} values are replaced by literature values[14,15] in eq 18, it results that $k_6 = 1.3 \times 10^4$ M^{-1} s^{-1} and 1.9×10^4 M^{-1} s^{-1} at 150.5 and 165.0 °C, respectively. The temperature dependence of k_6 values allows an estimation of 10 kcal mol^{-1} for the overall activation energy of the process represented by eq 6, which is a reasonable value.

If the main equations of the mechanism (4, 6, 7, 8, 13, and 16) are considered, if the AP decomposition takes place only through eq 9 and 10, and if the same values for the rate constants of the reactions represented by eq 7 and 8, are used, the following differential rate equation for the ACDP decomposition can be deduced (eq 19–21).

$$-\frac{d[\text{ACDP}]}{dt} = \left(k_1 + \frac{2\,k_1[\text{ACDP}]k_6}{k_6[\text{ACDP}] + (k_{13} + k_{16})[\text{benzene}]}\right)[\text{ACDP}] = k_{exp}[\text{ACDP}] \quad (19)$$

where

$$k_{exp} = k_1 + k_6\left(\frac{2\,k_1[\text{ACDP}]}{k_6[\text{ACDP}] + (k_{13} + k_{16})[\text{benzene}]}\right) \quad (20)$$

From eq 20 k_6 becomes

$$k_6 = \frac{(k_1 - k_{exp})(k_{13} + k_{16})[\text{benzene}]}{(k_{exp} - 3k_1)[\text{ACDP}]} \quad (21)$$

If the benzene concentration constant through the runs is considered, the k_{13} and k_{16} literature values[14-16] are substituted, and the k_1 and k_{exp} values given by Figure 1 are used, $k_6 = 5.10^4$ M^{-1} s^{-1} at 150.5 °C is obtained. (This value (± 8%) is an average of calculations made with ACDP initial concentrations higher than 0.2 mol kg^{-1}.)

The agreement between the k_6 values at 150.5 °C, calculated independently through eq 18 and 21, respectively, is quite satisfactory in view of the assumptions that have been made in each case.

(14) Buckley, R. P.; Leavitt, F.; Szwarc, M. *J. Am. Chem. Soc.* **1956**, *78*, 5557.
(15) Szwarc, M. *J. Polym. Sci.* **1955**, *16*, 367.
(16) Richardson, W. H.; Montgomery, F. C.; Slusser, P.; Yelvington, M. B. *J. Am. Chem. Soc.* **1975**, *97*, 2814.

Experimental Section

Materials. Acetone cyclic diperoxide (ACDP) was prepared[1a] by dropwise addition of acetone in acetonitrile to a vigorously stirred, cooled (−10 °C) solution of 69.7% hydrogen peroxide and sulfuric acid (18 M). After stirring for 1 h at −10 °C, filtration, thorough water washing, and drying, the crude product (71% yield) was purified by recrystallizing from ethyl acetate until a constant melting point was attained (132 – 132.5 °C [lit.[1,17] 133–135 and 132–133 °C]). The product purity was also checked by GC and IR analyses ((NaCl, Nujol) 2910 (s), 2850 (s), 1200 (m), 940 (w), 860 (w), 814 (w) and 682 (w) cm^{-1}). Acetyl peroxide (AP) was obtained according to the Slagle and Shine method.[18] The solid product was isolated at −78 °C, removing the solvent at reduced pressure. Methyl isopropyl ether was prepared by a standard method.[19] Organic solvents were purified with the appropriate techniques[20] and their purity was checked by GC analysis.

Kinetic Methods. Pyrex glass tubes (7 cm long × 6 mm exterior diameter) half filled with the appropiate ACDP solution, were thoroughly degassed in the vacuum line at −190 °C and then sealed with a flame torch. To perform the runs, they were immersed in the thermostatic oil bath (±0.1 °C) and withdrawn after selected times, stopping the reaction by cooling at 0 °C. Quantitative determinations of the ACDP remaining in the solutions were performed by GC analysis (see below) at 58 °C. The first-order rate constant values were calculated by a least mean square treatment of the reaction data, the activation parameters worked out from the Arrhenius plot, and the corresponding errors determined by the Schaleger and Long method.[21]

Product Analyses. The qualitative and quantitative determination of the organic reaction products was performed by GC programmed temperature analysis in 13% SE-30 Silicone Gum-Rubber stationary phase on Chromosorb-G, ($^1/_8$ in. exterior diameter) s.s. columns, installed in a 5840A-Hewlett-Packard Gas Chromatograph, using FID detection and nitrogen as carrier gas, and employing the internal standard method (chlorobenzene and *n*-octane). In some experiments, to separate the acetone and methyl isopropyl ether formed, a 25% β,β'-oxydipropionitrile stationary phase on Firebrick ($^1/_8$ in. × 6 ft) column was used. The oxygen and carbon dioxide products were analyzed in a Silica-Gel column with a TC detector and helium as carrier gas by injecting in the 5840A Instrument liquid samples of the ampoules' contents.

Acknowledgment. We thank Professor D. C. Nonhebel of Strathclyde University (Great Britain) for useful information about the synthesis of ACDP and the Dr. E. Castro group of this Institute for the theoretical calculations. INIFTA is sponsored by Consejo Nacional de Investigaciones Científicas y Técnicas, the Universidad Nacional de La Plata, and the Comisión de Investigaciones Científicas (Provincia de Buenos Aires).

Registry No. 3,3,6,6-Tetramethyl-1,2,4,5-tetraoxane, 1073-91-2; acetone, 67-64-1.

(17) Baeyer, A.; Villiger, V. *Chem. Ber.* **1899**, *32*, 3625.
(18) Slagle, J. R.; Shine, H. J. *J. Am. Chem. Soc.* **1959**, *24*, 107.
(19) Vogel, A. I. "A Text-book of Practical Organic Chemistry"; Longmans, Green and Co.: London, 1948.
(20) Riddick, J. A.; Bunger, W. B. In "Techniques of Chemistry"; Weissberger, A., Ed.; Wiley: New York, 1970; Vol. II.
(21) Schaleger, L. L.; Long, F. A. *Adv. Phys. Org. Chem.* **1963**, *1*, 1.