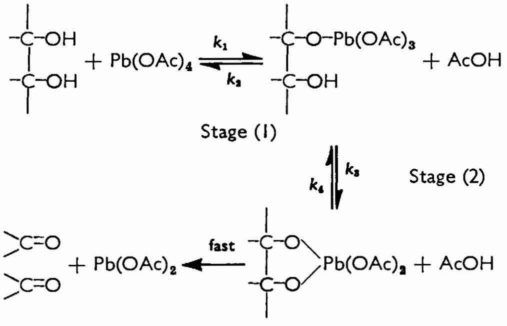
799. *Oxidations with Iodosobenzene Diacetate. Part VIII.* A Kinetic Study of the Oxidation of Benzpinacol.*

By L. K. Dyall and K. H. Pausacker.

Benzpinacol has been oxidised with iodosobenzene diacetate in both acetic acid–benzene and acetic acid–nitrobenzene between 16·30° and 66·65°. The enthalpies and entropies of activation, which varied appreciably as the composition of each mixed solvent was altered, were found to be linearly related, and the same solvent isokinetic relationship was obeyed in both solvent systems. The existence of isokinetic relationships in other glycol oxidations is discussed.

From a kinetic study of the oxidation of 1 : 2-diols with lead tetra-acetate in several solvents, Criegee, Kraft, and Rank[1] deduced mechanism (A) for the reaction. Since *cis*-diols would form a cyclic intermediate more readily than *trans*-diols, the fact that *cis*-diols are usually oxidised more rapidly than *trans*-diols can be explained if stage (2) is assumed to be rate-determining.



Mechanism (A)

The equilibrium constant, K, for stage (1) is given by

$$K = [\text{AcOH}][\text{monoester}]/[\text{glycol}][\text{Pb(OAc)}_4]$$

whence $$[\text{monoester}] = K\,[\text{glycol}][\text{Pb(OAc)}_4]/[\text{AcOH}]$$

If $k_1 \sim k_2 \gg k_3 \gg k_4$, it follows that the rate of oxidation, k, is given by

$$k = \text{const.} \times K[\text{glycol}][\text{Pb(OAc)}_4]/[\text{AcOH}] \quad . \quad . \quad . \quad . \quad . \quad (1)$$

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* Part VII, *Austral. J. Chem.*, 1957, **10**, 460.

[1] Criegee, Kraft, and Rank, *Annalen*, 1933, **507**, 159.

Relation (1) predicts that, if the concentration of acetic acid is reduced, the rate of oxidation will be increased, and partial confirmation was obtained by Criegee *et al.*[1] When a substantial proportion of an acetic acid solvent was replaced by benzene, nitrobenzene, dichloroethane, or tetrachloroethane, the rate of oxidation of *cyclo*hexane-1 : 2-diol was markedly increased. Later, Büchner and Criegee [2] found that addition of small amounts of water or methanol to an acetic acid solvent increased the rate of oxidation far more than could be accounted for by relation (1). It was suggested that, in these instances, lead tetra-acetate was solvolysed to a more active oxidant [Mechanism (B)]. Hydroxylic solvents able to react with the oxidant in this way were termed " active," while solvents unable so to react were termed " inert."

$$\mathrm{Pb(OAc)_4 + 2ROH \rightleftharpoons Pb(OAc)_2(OR)_2 + 2AcOH}$$

Mechanism (B)

If a 1 : 2-diol is oxidised in an inert solvent containing an excess of acetic acid, relation (1) predicts that the rate of oxidation is inversely proportional to the concentration of acetic acid. The present work was carried out to test the quantitative validity of this relation. Benzpinacol was oxidised in acetic acid–benzene and acetic acid–nitrobenzene solvents of varied composition. Benzene (dielectric constant $\varepsilon = 2{\cdot}38$) and nitrobenzene ($\varepsilon = 37{\cdot}8$) were chosen as the inert solvents to ensure that the changes in rate due to changes in the concentration of acetic acid ($\varepsilon = 9{\cdot}7$) could be differentiated from changes in rate due to variation of the dielectric constant of the solvent. It was found convenient to study the rates of oxidation with iodosobenzene diacetate; lead tetra-acetate and iodosobenzene diacetate are very similar in their action on 1 : 2-diols.[3,4,5]

EXPERIMENTAL

Purification of Materials.—Acetic acid was successively treated with chromic oxide and boron triacetate.[6] The anhydrous acid (m. p. 16·60°) thus prepared was too hygroscopic for convenient use, and was therefore diluted with distilled water to a water content of 0·15% by weight (m. p. 16·40°). Acrylonitrile was redistilled, b. p. 78°, immediately before use. Benzene was purified by Vogel's method [7] and dried over sodium wire.

Benzpinacol, prepared from benzophenone and propan-2-ol,[8] was crystallised three times from benzene–ligroin and had m. p. 188—189°. Iodosobenzene diacetate, prepared by Pausacker's method [3] and crystallised from benzene, had a minimum purity of 99·5%. The purity was checked at weekly intervals. Nitrobenzene, thoroughly washed with 2N-sodium hydroxide and distilled water in succession, was dried ($CaCl_2$) and distilled; b. p. 51°/0·1 mm., n_D^{15} 1·346.

TABLE 1. *Yield of benzophenone from the oxidation of benzpinacol with iodosobenzene diacetate in various solvents.*

	Inert solvent (ml.)	Acetic acid (ml.)	Benzophenone (yield %)
Benzene	50	0	96
	40	10	100
	25	25	84
	0	50	86
Nitrobenzene	45	5	91

Analysis of Products.—Benzpinacol (0·500 g.; 0·00137 mole) was oxidised, at room temperature, with iodosobenzene diacetate (0·490 g.; 0·00152 mole) in 50 ml. of the solvent of required composition. The course of the oxidation was followed by periodically removing a 1 ml. portion, adding it to acidified potassium iodide, and titrating the liberated iodine with

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[2] Büchner and Criegee, *Ber.*, 1940, **73**, 563.
[3] Pausacker, *J.*, 1953, 107.
[4] Beucker and Criegee, *Ber.*, 1939, **541**, 218.
[5] Criegee, Höger, Huber, Kruck, Marktscheffel, and Schellenberger, *Annalen*, 1956, **599**, 81.
[6] Eichelberger and LaMer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.
[7] Vogel, " A Text Book of Practical Organic Chemistry," Longmans, London, 1950, p. 171.
[8] " Organic Syntheses," Wiley, New York, 1946, Coll. Vol. II, p. 71.

standardised sodium thiosulphate. When oxidation was complete, acetic acid and benzene were distilled off, and the oily residue of benzophenone and iodobenzene was crystallised from aqueous methanol or propan-2-ol. The benzophenone obtained was identified by determination of the m. p. and mixed m. p. When nitrobenzene was present the reaction mixture was treated with the theoretical quantity of 2 : 4-dinitrophenylhydrazine. Part of the expected yield of benzophenone 2 : 4-dinitrophenylhydrazone (m. p. and mixed m. p., 240—241°) crystallised, and the remainder was recovered by distilling off the solvent at reduced pressure and crystallising the residue from ethanol. The results of these analyses are given in Table 1.

Kinetic Procedure.—The temperature of the thermostat was controlled within ±0·03° if below 40°, or within ±0·12° if 40° or higher. The analytical procedure used was essentially that of Cordner and Pausacker.[10] The first aliquot portion was removed 5—10 min. after mixing the preheated reactants, and the remaining eight portions were removed at intervals such that the reaction was followed from 15 to 60% completion. The time of half-outflow of the first portion into acidified potassium iodide was taken as zero time.

TABLE 2.

% AcOH (by vol.)	10^3k (mole^{-1} l. sec.$^{-1}$)					E (kcal. mole^{-1})	$\log_{10} A$	$\Delta F^{\ddagger}$ (kcal. mole^{-1})	$\Delta H^{\ddagger}$ (kcal. mole^{-1})	$-\Delta S^{\ddagger}$ (cal. deg.$^{-1}$)
	16·30°	25·65°	35·10°	40·04°	45·17°					
(a) *Oxidation in acetic acid–benzene solvents*										
4	3·16	5·00	10·3	12·8	16·9	10·96	5·76	20·56	10·37	34·17
	3·34	5·37	11·5	13·7	16·8					
6	2·90	5·24	10·8	13·7	16·6	11·69	6·27	20·58	11·10	31·80
	2·85	5·31	10·0	13·7	17·3					
8	2·47	4·58	9·84	13·9	17·6	12·93	7·14	20·65	12·34	27·87
	2·47	4·90	10·2	14·6	17·6					
10	2·08	4·02	9·31	13·6	17·4	13·41	7·44	20·72	12·82	26·50
	1·98	4·07	9·69	13·1	17·6					
16	1·21	2·82	7·16	10·9	15·9	17·16	10·00	20·99	16·57	14·82
	1·11	2·81	7·03	10·7	14·9					
20	0·753	2·35	5·51	9·38	13·7	18·30	10·71	21·15	17·71	11·54
	0·806	2·16	5·65	8·89	13·4					
30	—	1·22	3·43	5·53	9·31	20·71	12·19	21·53	20·12	4·729
		1·25	3·48	5·72	9·37					
40	—	0·777	2·13	3·53	6·11	23·69	14·09	21·93	23·10	−3·924
		0·722	2·10	3·53	6·10					
60	—	—	—	1·73	3·13 *	21·36	12·17	22·11	20·77	4·494
				1·82	3·08 *					
100	—	—	—	1·82	2·67 †	21·15	11·99	22·24	20·56	5·601
				1·81	2·74 †					
(b) *Oxidation in acetic acid–nitrobenzene solvents*										
4	—	1·40	2·84	3·71	6·32	14·17	7·50	21·40	13·58	26·23
		1·31	2·81	3·92	5·72					
10	—	1·73	3·72	5·11	7·08	13·80	7·35	21·23	13·21	26·90
		1·77	3·66	5·61	7·21					
16	—	2·14	4·59	6·94	9·15	13·68	7·36	21·09	13·09	26·83
		2·32	4·66	6·54	8·85					
			4·81							
20	—	2·36	5·45	8·25	10·7	14·27	7·84	21·03	13·68	24·65
		2·40	5·47	7·81	9·81					
				8·05						
30	—	3·05	6·79	12·0	17·6	17·48	10·26	20·94	16·89	13·58
		2·97	7·61	13·7	16·9					
40	—	3·08	8·39	11·5	22·0	18·35	10·93	20·89	17·76	10·50
		3·30	8·67	11·9	23·6					
60	—	3·62	8·02	12·7	20·1	18·74	11·19	20·92	18·15	9·29
		3·76	8·19	13·2	19·9					
80	—	1·71	4·38	8·01	13·3	19·77	11·69	21·27	19·18	7·01
		1·76	4·54	7·71	13·3					

* At 56·15°, 10·7, 10·4; at 66·65°, 26·4, 25·6. † At 56·15°, 9·82, 10·5; at 66·65°, 24·3, 23·5.

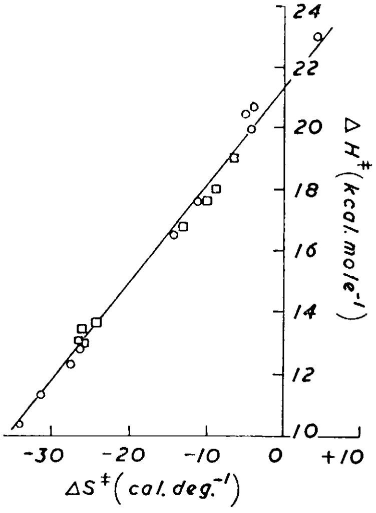
A solution of the oxidant in the solvent of composition used in the kinetic run was titrated before and after each run to check the stability of the oxidant; the deviation between the two titres never exceeded 0·5%.

Calculations.—A second-order rate constant was calculated for each aliquot portion titrated, and the arithmetic mean of the set of values was obtained. Variations from the mean were of a random nature, and did not exceed 5%.

The energy of activation, E, and the frequency factor, A, were calculated from the Arrhenius relationship by the method of least squares, and the enthalpy, $\Delta H^{\ddagger}$, free-energy change, $\Delta F^{\ddagger}$, and entropy, $\Delta S^{\ddagger}$, of activation at 25° were calculated by standard methods. By using these values of A and E, rate constants for each run were calculated from the Arrhenius equation; the mean deviation from the experimental values was 4·9% for acetic acid–benzene and 3·4% in acetic acid–nitrobenzene solvents. The results for both types of solvent are presented in Table 2.

Pure-order kinetics were not obtained when pure benzene or nitrobenzene was used as solvent; this is in agreement with observations by Criegee, Kraft, and Rank.[1]

Polymerisation Tests with Acrylonitrile.—The following mixtures were prepared: (i) A solution of benzpinacol (0·40 g.) and iodosobenzene diacetate (0·30 g.) in acetic acid (5 ml.), acrylonitrile (15 ml.), and benzene (30 ml.). (ii) A mixture of acetic acid (5 ml.), acrylonitrile (15 ml.), and benzene (30 ml.). (iii) A solution of benzpinacol (0·40 g.) in acetic acid (5 ml.), acrylonitrile (15 ml.), and benzene (30 ml.). (iv) A solution of iodosobenzene diacetate (0·30 g.) in acetic acid (5 ml.), acrylonitrile (15 ml.), and benzene (30 ml.).



○ Acetic acid–benzene: β = 320·8° K, $\Delta H_0^{\ddagger}$ = 21·59 kcal. mole^{-1}.

☐ Acetic acid–nitrobenzene: β = 310·4° K, $\Delta H_0^{\ddagger}$ = 21·42 kcal. mole^{-1}.

The four solutions were kept in a thermostat at 45° for 1·5 hr. and then cooled to room temperature. Dry, peroxide-free ether was added to precipitate any polymerised acrylonitrile. White precipitates of the polymer settled from solutions (i) and (iv) only on standing overnight. Dilution with ether did not precipitate a polymer from either of these two solutions if the monomeric acrylonitrile was extracted with distilled water immediately after the period at 45°. Polymerisation therefore occurs only on prolonged contact with the oxidant, and not during the oxidation of the glycol.

DISCUSSION

The relation (1) can now be tested. At a constant temperature, and at constant concentrations of benzpinacol and iodosobenzene diacetate, relation (2) should be obeyed.

$$k_V = k_{100} \times 100/V \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

k_V and k_{100} are the rates of reaction in solutions containing V% (v/v) and 100% acetic acid, respectively. Calculated values of k_V at 16·30° for acetic acid–benzene, and at 25·63° for acetic acid–nitrobenzene solvents, are shown in Table 3.

In acetic acid–benzene solvents, although the rate of reaction increases steadily as acetic acid is replaced by benzene, this increase is less than the calculated increase at concentrations greater than 40% (vol.) acetic acid, while at lower acetic acid concentrations the rates are higher than expected. In acetic acid–nitrobenzene solvents the observed rate initially increases much more rapidly than that calculated but, as the acetic acid concentration decreases further, the observed rates actually diminish. Agreement between $k_{\text{obs.}}$ and k_V is no better at other temperatures. The effect of acetic acid concentration is therefore not as simple as predicted by relation (2). Evidently acetic acid exerts appreciable solvation effects in addition to the predicted mass-action effect. Since the mechanism of the oxidation is not known with certainty, and kinetic measurements were made in the vicinity of the isokinetic temperature (see later), it is not possible to correlate solvent composition and oxidation rate.

TABLE 3. *Experimental and calculated rate constants in mixed solvents.*

Acetic acid–benzene (16·30°)						Acetic acid–nitrobenzene (25·63°)					
AcOH (vol. %)	$10^4k_{\text{obs.}}$	10^4k_V	AcOH (vol. %)	$10^4k_{\text{obs.}}$	10^4k_V	AcOH (vol. %)	$10^4k_{\text{obs.}}$	10^4k_V	AcOH (vol. %)	$10^4k_{\text{obs.}}$	10^4k
4	30·6	26·5	20	7·82	5·29	4	13·6	84·0	40	31·9	8·40
6	28·2	17·7	30	3·60	3·52	10	17·5	33·5	60	36·9	5·60
8	24·0	13·2	40	1·59	2·66	16	22·3	21·0	80	17·4	4·20
10	20·9	10·6	60	1·10	1·76	20	23·8	16·8	100	3·35	(3·35)
16	10·7	6·63	100	1·06	(1·06)	30	30·1	11·2			

In acetic acid–benzene solvents, $\log_{10} A$ varies from 5·76 to 14·09 (see Table 2), accompanied by corresponding changes in E (10·96—23·70 kcal. mole^{-1}). The relationship between $\log_{10} A$ and E is in fact linear, and a similar relationship exists in acetic acid–nitrobenzene solvents (Table 2) where $\log_{10} A$ varies from 7·35 to 11·99, and E from 13·68 to 21·15 kcal. mole^{-1}. These linear relationships indicate that a solvent isokinetic relationship [9] exists in each instance. In each solvent system, the enthalpy and entropy also vary over a wide range of values, and the relationship between these quantities is linear. The linearity of the plot has been tested for each mixed solvent system by evaluation of the correlation coefficient, r. The approximation of r to unity ($r = 0{\cdot}996$ in acetic acid–benzene solvents and 0·946 in acetic acid–nitrobenzene solvents) establishes the linearity beyond doubt.[9] The linear relationship may be expressed by equation (3) in acetic acid–benzene, and by equation (4) in acetic acid–nitrobenzene solvents.

$$\Delta H^{\ddagger} = 21{\cdot}59 + 320{\cdot}8\,\Delta S^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\Delta H^{\ddagger} = 21{\cdot}42 + 310{\cdot}4\,\Delta S^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The linear enthalpy–entropy ("isokinetic") relationship has recently been discussed by Leffler,[9] who showed that the two variables are correlated by equation (5).

$$\Delta H^{\ddagger} = \Delta H_0^{\ddagger} + \beta\,.\,\Delta S^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

β is known as the isokinetic temperature, and at this temperature all reactions obeying the same isokinetic relationship will proceed at the same rate. β and the intercept $\Delta H_0^{\ddagger}$ have been calculated by the method of least squares for both solvent systems. The differences between the two isokinetic temperatures (48° in acetic acid–benzene solvents, 37° in acetic acid–nitrobenzene solvents) and the $\Delta H_0^{\ddagger}$ values (21·59 and 21·42 kcal. mole^{-1}, respectively) do not exceed the experimental errors, and it can be concluded that the same isokinetic relationship is obeyed in both solvent systems. The isokinetic temperature is actually within the temperature range at which the rate constants were measured, and the variations in rate as the solvent composition varied cannot therefore be regarded as significant.[9]

The kinetic data from several other investigations of the oxidation of glycols appear to obey isokinetic relationships. It is predicted by Büchner and Criegee's mechanism (B) that progressive addition of water to an acetic acid solvent should be accompanied by increases in the rate of oxidation of a 1 : 2-diol with lead tetra-acetate. Cordner and

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[9] Leffler, *J. Org. Chem.*, 1955, **20**, 1202.

Pausacker,[10] however, found that the rate of oxidation of ethylene glycol increased to a maximum and then decreased as more water was added. The $\log_{10} A$ (10·96—14·51) and E (17·8—23·4 kcal. mole^{-1}) values are approximately linearly related, and, since the isokinetic temperature (60°) is in the vicinity of the temperatures (18—35°) at which kinetic measurements were made, a simple relationship between oxidation rate and solvent composition should not be expected. It is not certain that this is a solvent isokinetic relationship, since progressive addition of water to the acetic acid solvent may cause corresponding changes in the structure of the oxidant [Mechanism (B)].

The oxidation of pinacols with lead tetra-acetate in acetic acid solution [10] also appears to obey a structural isokinetic relationship ($\log_{10} A$, 10·52—14·87; E, 13·4—23·2 kcal. mole^{-1}). As the isokinetic temperature (95°) is well removed from the temperatures (18—35°) at which kinetic measurements were made, discussion of these results is probably valid.

An outstanding example of a structural isokinetic relationship is provided by the kinetic data obtained by Moriconi, O'Connor, and Wallenberger [11] for the oxidation of *cis*- and *trans*-9 : 10-diaryl-9 : 10-dihydrophenanthrene-9 : 10-diols. The $\log_{10} A$ values vary from 7·75 to 16·18, and E varies from 7·7 to 20·5 kcal. mole^{-1}. If the recalculated value of $A = 1{\cdot}42 \times 10^{15}$ for one *cis*-diol is used instead of the incorrect value of $1{\cdot}26 \times 10^{10}$ quoted by Moriconi *et al.*, the plot of $\log_{10} A$ versus E is linear. The isokinetic temperature (—25°) is 45—55° away from the temperatures used for the calculation of A and E values, and the detailed correlation between oxidation rate and diol structure made by these authors is therefore probably valid.

Isokinetic relationships may therefore be responsible for some of the difficulties [5] in correlating glycol structure or solvent composition with oxidation rate. Discussions based on rate constants determined at only one temperature, in the vicinity of the isokinetic temperature, are pointless if isokinetic relationships are obeyed by the reactions in question.

The mechanism of glycol oxidations has recently received considerable attention. The mechanism we previously suggested [10] involved initial condensation between the glycol and the oxidant to form a glycol monoester, followed by homolytic fission of the ester and abstraction of the remaining hydroxyl-group hydrogen atom of the glycol. Hey, Stirling, and Williams [12] have criticised this mechanism on the grounds that quantitative oxidation of glycols with iodosobenzene dibenzoate and lead tetrabenzoate occurs at temperatures much lower than those at which these oxidants are able to phenylate aromatic compounds. Moreover, the homolytic fission of the glycol ester would produce a radical more likely to attack the carbon-bound hydrogen atoms of the glycol than the hydrogen atom of a hydroxyl group. The first criticism may not be valid, since homolytic decomposition of the ester of the glycol with the oxidant is not strictly analogous to similar decomposition of the oxidant. The second objection is, however, a strong one, and appears to be supported by our failure to detect free radicals with acrylonitrile monomer during the oxidation of benzpinacol with iodosobenzene diacetate. It is also known now that hydrogen bonding of the glycol hydroxyl groups does not play a significant rôle.[5,11,13,14] We now suggest that the separation of the lead triacetoxy-group [see Mechanism (C)] is concomitant with attack on the adjacent hydroxyl group of the glycol. This mechanism is essentially an electron redistribution within a cyclic complex, and the distinction between homolytic and heterolytic fission is too fine to be drawn.[15,16]

Since a cyclic transition state involving both glycol hydroxyl groups is involved, this mechanism accounts for the observation that the ratio, k_{cis}/k_{trans}, of rates of oxidation of

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[10] Cordner and Pausacker, *J.*, 1953, 102.

[11] Moriconi, O'Connor, and Wallenberger, *J. Amer. Chem. Soc.*, 1958, **80**, 656.

[12] Hey, Stirling, and Williams, *J.*, 1954, 2747.

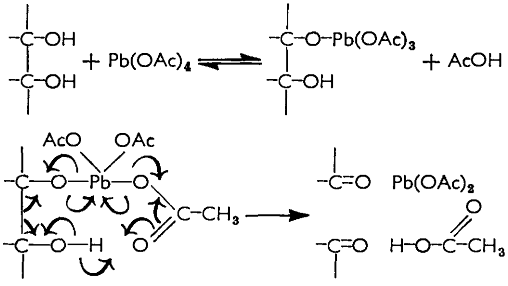
[13] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492; 1954, **76**, 4323.

[14] Kuhn, Moriconi, O'Connor, and Wallenberger, *J. Org. Chem.*, 1957, **22**, 1651.

[15] Hughes and Ingold, *Quart. Reviews*, 1952, **6**, 34.

[16] Buist and Bunton, *J.*, 1954, 1406.

isomeric *cis*- and *trans*-glycols is usually greater than unity. It is not suggested, however, that this mechanism accounts for the oxidation of all glycols, and recent work by Levesley, Waters, and Wright[17] indicates that the ratio k_{cis}/k_{trans} is not always significant.



Mechanism (C)

The Brönsted-base mechanism (Criegee *et al.*,[5] Moriconi *et al.*,[11] Bell, Rivlin, and Waters[18]) is an alternative reaction path.

One of us (L. K. D.) is indebted to the Dunlop Rubber Company of Australia for a research scholarship.

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[*Received, May* 15*th*, 1958.]

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[17] Levesley, Waters, and Wright, *J.*, 1956, 840.
[18] Bell, Rivlin, and Waters, *J.*, 1958, 1696.