# THE VELOCITY COEFFICIENTS OF THE CHAIN **PROPAGATION AND TERMINATION REACTIONS** IN OLEFIN OXIDATIONS IN LIQUID SYSTEMS

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The purpose of this new investigation of the kinetics of the liquid phase oxidation of olefins was twofold: (1) to study more completely the relative importance of the three termination reactions; (2) to try by improved experi-mental techniques to obtain more reliable estimates of the absolute velocity coefficients.

It is shown that the cross termination process, between unlike radicals, is relatively more favoured in the more reactive olefins. In contrast to copolymerizations,<sup>11</sup> where only substituted-alkyl radicals are involved, no value of  $\phi$  very much greater than I has been found, and in one example a fractional value was actually observed.

New estimates of the velocity coefficients still leave much to be desired in They show little variation between the magnitude of the different accuracy. radical-radical reactions, and in this respect oxygen behaves as a radical.

Non-conjugated olefins in the liquid phase at moderate temperatures absorb oxygen to form hydroperoxides by the following radical chain reaction mechanism : 1

Initiation :	Production of R <sup>-</sup> or $RO_2^-$ radicals $r_i$				(1)
Propagation :	$R^- + O_2 \rightarrow$	RO <sub>2</sub> -	$k_2$	•	(2)
	$\mathrm{RO}_2$ + RH $\rightarrow$	$RO_{2}H + R^{-}$	$k_{3}$		(3)
Termination :	$2R^- \rightarrow $		k <sub>4</sub>		(4)
	$\mathrm{R}^- + \mathrm{RO}_2^- \rightarrow$	Non-initiating	$k_{5}$		(5)
	$2 \text{RO}_2^- \rightarrow$	producto,	k <sub>6</sub>		(6)

where RH represents the olefin, R- the radical obtained on removal of an  $\alpha$ -methylenic hydrogen atom H,  $r_i$  is the rate of initiation, and the k's are the respective velocity coefficients of the reactions indicated. There are two uncertainties in the earlier kinetic analysis : (i) the absolute magnitude of  $r_{i}$ , i.e. for example, its relationship to the overall rate of decomposition of a free radical producing catalyst such as benzoyl peroxide and (ii) the validity of the assumption made hitherto that  $k_{5}^{2} = k_{4}k_{6}$ . This paper is mainly concerned with investigating (ii) and with evaluating the velocity coefficients on a more general kinetic basis. The absolute values deduced for these coefficients necessarily depend on (i), and here certain inconsistencies remain to be resolved. Our results assume that in benzoyl peroxide catalyzed oxidations each molecule of peroxide decomposing initiates one chain.<sup>2</sup>

Stationary State Relationships for the Generalized Kinetic Scheme.-A complete kinetic analysis of the set of reactions listed above leads to a complex and intractable rate equation, which, however, can be greatly simplified by introducing the single assumption, valid if the chain length is long, that

$$k_2[R^-][O_2] = k_3[RH][RO_2^-]$$
. . . (1)

<sup>1</sup> Bolland, *Quart. Rev.*, 1949, **3**, 1. <sup>2</sup> Bolland and ten Have, *Trans. Faraday Soc.*, 1947, **43**, 201.

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The rate of oxidation r can then be expressed in terms of three composite constants defined by

$$\begin{array}{c} A = k_2 k_4^{-\frac{1}{2}} \\ B = k_3 k_6^{-\frac{1}{2}}, \\ \phi = k_4^{-\frac{1}{2}} k_5 k_6^{-\frac{1}{2}} \end{array} \right\} \qquad . \qquad . \qquad . \qquad (2)$$

The result is

$$r = r_{\infty} \{ \mathbf{I} + 2\phi A^{-1}B [RH] [O_2]^{-1} + A^{-2}B^2 [RH]^2 [O_2]^{-2} \}^{-\frac{1}{2}}, \quad . \quad (3)$$

where the limiting rate at sufficiently high oxygen pressures is given by

If  $\phi = 1$ , as hither to assumed, eqn. (3) reduces to

In this case, a plot of  $r^{-1}$  against  $[O_2]^{-1}$  will be linear, and the constants A and B are obtainable from the slope and intercept. Data consistent with this relationship have been published 3, 4, 5 and used to evaluate A and B.

More critical consideration of eqn. (3) shows that a plot of  $r^{-1}$  against  $[O_2]^{-1}$  will be concave to the latter axis if  $\phi < I$  and convex if  $\phi > I$ , but that so long as  $\phi$  does not differ greatly from unity, it would not be easy experimentally to observe the curvature by measurements in the pressure range ( $\leq 5$  mm.) normally employed in earlier work. It is also readily seen that if eqn. (5) is wrongly employed when  $\phi \neq 1$  the constant deduced as A is actually more nearly equal to  $k_2k_5^{-1}k_6^{\frac{1}{2}}$ . Values previously listed 4, 5, 8 for  $k_2 k_4^{-\frac{1}{2}}$  are therefore open to suspicion, and we shall in fact show below that some of them are in need of considerable revision.

### Determination of $\phi$

Materials .-- The preparation and purification of ethyl linoleate, ethyl linolenate, methyl oleate and 2:6:11:15-tetramethylhexadeca-2:6:10:14tetraene (digeranyl) have been indicated elsewhere.<sup>7,8</sup> Hexadec-I-ene,  $n_D^{so}$ 1.4419, was obtained by fractionating a commercial sample through a 15-plate column. Phytene,  $n_D^{20}$  1.4515, was prepared by reducing phytol in liquid ammonia with sodium and alcohol. All specimens were examined spectroscopically; phytene was thus found to contain 3 % of its less reactive  $\Delta^{1}$ -isomer, and the hexadecene contained 2 % of its  $\Delta^{2}$ -isomer. Immediately before use, any adventitious peroxidic or other polar impurities were removed by running petrol solutions through a 15 cm. alumina column.

Azobis(isobutyronitrile) was recrystallized from methanol. Benzoyl peroxide was purified by several precipitations from chloroform solution by methanol. These catalysts were introduced into the reaction vessel in acetone solution, the

solvent then being evaporated off in a stream of nitrogen. Apparatus.—The constant pressure gas burette system described by Bolland<sup>9</sup> was used with minor modifications. At very low pressures, the constant pressure control lacked sensitivity and manual control using the octoil (octyl phthalate) manometer as indicator was adopted.

**Procedure.**—A series of rate measurements (r) at oxygen pressures varying from 0.4 to 50 mm. were made on the same sample of olefin plus catalyst. The series was interspersed with measurements  $(r_1)$  at a standard pressure (generally 20 mm.) in order that any change in  $r_1$  due to autocatalysis or catalyst decomposition could be allowed for. A plot of  $r_1/r$  against  $[O_2]^{-1}$  was extrapolated to  $[O_2]^{-1} = 0$  to obtain  $r/r_{\infty}$ . Then, according to eqn. (3), a plot of  $\{(r_{\infty}/r)^2 - I\}[O_2]$ 

- <sup>3</sup> Bolland, Trans. Faraday Soc., 1948, 44, 669.
- <sup>4</sup> Bolland and ten Have, Trans. Faraday Soc., 1949, 45, 93.
- <sup>5</sup> Bamford and Dewar, Proc. Roy. Soc. A, 1949, 198, 252.
- <sup>6</sup> Bateman and Gee, Trans. Faraday Soc. (in press).
- <sup>7</sup> Bolland, Trans. Faraday Soc., 1950, 46, 358.
  <sup>8</sup> Bateman, Bolland and Gee, Trans. Faraday Soc. (in press).
- <sup>9</sup> Bolland, Proc. Roy. Soc. A, 1946, 196, 218.

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against  $[O_2]^{-1}$  should then be a straight line of slope  $A^{-2}B^2[RH]^2$  and ordinate intercept  $2\phi A^{-1}B[RH]$ . From these two quantities, and making use of eqn. (4), we can evaluate the three constants A, B and  $\phi$ .

In the above equations  $[O_2]$  represents the concentration of oxygen in the liquid, and is related to the gaseous oxygen pressure p by

where  $\beta$  is the solubility of oxygen in the olefin in moles 1.<sup>-1</sup> (mm. Hg)<sup>-1</sup> and  $k_s$  a shaking constant. The latter was determined for the present experimental conditions as described by Bateman, Bolland and Gee,<sup>8</sup> by a method independent of  $\phi$ , and eqn. (6) then used to calculate  $[O_2]$  from the measured p.

In the early part of this work, benzoyl peroxide was used as the initiating agent, but evidence was found of a variation in its efficiency with oxygen pressure apparent at low pressures. This, together with uncertainty concerning the amount of carbon dioxide evolved per mole decomposed were soon found to present serious difficulties. Azobis(isobutyronitrile) was therefore used subsequently to obtain all the results reported in this section of the paper. The small values of r encountered at the lower pressures necessitated corrections for the amount of nitrogen evolved by the catalyst; these were as much as 0.1 r at the lowest pressure. Nitrogen evolution, which is stoichiometric, was measured in ethyl linoleate solution in vacuo and its rate at  $45^{\circ}$  was found to agree with published data  $1^{\circ}$  to within 1 %, i.e.  $k = 1.06 \times 10^{-6}$  sec.<sup>-1</sup>. There was no evidence to suggest that dilution of the gaseous oxygen by the liberated nitrogen introduced any spurious effects. On the basis that each mole of catalyst decomposing initiates one chain (and this is certainly to high an estimate), the chain lengths at the lowest oxygen pressure varied from 9 to 40 for the east and most active olefin studied, respectively.

#### Results

Fig. I shows plots of  $r_{\infty}/r$  against  $[O_2]^{-1}$  for ethyl linoleate catalyzed by (a) azobis(isobutyronitrile) and (b) benzoyl peroxide. Fig. 2 gives similar plots for phytene, methyl oleate and hexadec-I-ene. The marked curvature of some of these plots shows that  $\phi$  differs from unity. In Fig. 3 and 4 are given the derived plots of  $\{(r_{\infty}/r)^2 - 1\}[O_2]$  against  $[O_2]^{-1}$ . A satisfactory linear relationship evidently exists in the nitrile catalyzed systems—and this applies also to the other olefins examined (Table I)—and serves to establish that eqn. (1) accurately describes the dependence of r on  $[O_2]$ . The departure from linearity at low values of  $[O_2]$  when benzoyl peroxide is used as catalyst (Fig. 3b) undoubtedly reflects the variations in catalytic efficiency referred to above.

Olefin	Unsaturation Pattern		$10^{-3} k_2 k_4^{-\frac{1}{2}}$ mole $-\frac{1}{2}$ l. $\frac{1}{2}$ sec. $-\frac{1}{2}$
Ethyl linolenate	$. CH : CH . CH_2 . CH : CH . CH_2 . CH : CH .$	3.3	1.3
Ethyl linoleate	$. CH : CH . CH_2 . CH : CH .$	2.5	1.6
Digeranyl .	$. CMe : CH . CH_2 . CH_2 . CMe : CH .$	3.1	0.9
Phytene	$. CH_2 . CMe : CH . CH_3 .$	I *	0.40
Methyl oleate .	. CH <sub>2</sub> . CH : CH . CH <sub>2</sub> .	0.3	0.23

TABLE I

\* On the basis of the  $r_{\infty}/r$  against  $[O_2]^{-1}$  plot.

Values of  $\phi$  and  $k_2k_4^{-\frac{1}{2}}$  for five olefins at 45° C are given in Table I. It proved impossible to determine these quantities for hexadec-1-ene because its rate of oxidation is insensitive to diminishing oxygen pressure above 0.5 mm. (Fig. 2). Comparison of this behaviour with that of ethyl linoleate, for example, affords a striking demonstration of the influence of olefinic structure. The pressure insensitivity of the oxidation rate of the former is readily understandable in

<sup>10</sup> Matheson, Auer, Bevilacqua and Hart, J. Amer. Chem. Soc., 1949, 71, 2610.

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view of the low reactivity of RH and correspondingly high reactivity of R-, these two factors operating in the same direction.

The validity of the original assumption that

$$k_{5} = k_{4}^{\frac{1}{2}}k_{6}^{\frac{1}{2}}$$

is obviously justified to a first approximation by the magnitude of the  $\phi$ 's given in Table I. Notwithstanding this, a definite trend in the values is apparent, viz., the more reactive the olefin (at high oxygen pressures), the higher the  $\phi$ .



**Non-Stationary State Relationships** 

To proceed further, it is necessary to make observations of the photochemical oxidation during the non-stationary period when the light has just been switched on or off. Such measurements can lead to the evaluation of two further composite constants :

$$b = k_2/k_4$$
;  $D = k_3/k_6$ . . . . (7)

These, together with A, B and  $\phi$  permit the five individual velocity constants to be calculated.

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The photochemical after-effect has been discussed by Bateman and Gee (compare Bamford and Dewar) who define the "decay intercept"  $I_d$  by

where  $r_D$  is the rate of the stationary dark reaction and t is the time



measured from the instant of switching off the light (cf. Fig. 5). Similarly a "growth intercept"  $I_g$  is defined by

$$I_{g} \equiv \int_{0}^{\infty} (r_{L} - r) dt, \quad . \quad . \quad . \quad (9)$$

where  $r_L$  is the rate of the stationary light reaction, and t the time of illumination.

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By an extension of the method of Bateman and Gee to the more general kinetic system discussed above, these intercepts may be evaluated as

$$I_{d} = a \ln \left( \frac{\gamma_{L} + \gamma_{D}}{2\gamma_{D}} \right), \quad . \quad . \quad . \quad (10)$$

$$I_{g} = a \ln \left( \frac{2r_{L}}{r_{L} + r_{D}} \right), \quad . \quad . \quad . \quad (11)$$

$$a = \frac{D[\mathrm{RH}] + A^{-2}B^{2}C[\mathrm{RH}]^{2}[\mathrm{O}_{2}]^{-1}}{1 + 2\phi A^{-1}B[\mathrm{RH}][\mathrm{O}_{2}]^{-1} + A^{-2}B^{2}[\mathrm{RH}]^{2}[\mathrm{O}_{2}]^{-2}} \qquad .$$
(12)

For reasons already advanced • and further discussed below, the experimental observations are best analyzed as the difference of these two intercepts, i.e.

$$I_{\mathbf{d}} - I_{\mathbf{g}} = a \ln \frac{(\mathbf{r}_{\mathbf{L}} + \mathbf{r}_{\mathbf{D}})^2}{4^{\mathbf{r}} \mathbf{L}^{\mathbf{r}} \mathbf{D}} \qquad . \qquad . \qquad (13)$$

We have therefore used this equation to evaluate a. The denominator of the expression for a (eqn. (12)) will be recognized as the main term of eqn. (3), and is entirely determined from stationary state data. This cumulify multiplied by a is

quantity, multiplied by a is, according to eqn. (12), a linear function of  $[O_2]^{-1}$ , the slope and intercept determining C and D respectively.

Bateman, Bolland and Gee<sup>8</sup> have measured the photochemical pre- and after-effects in oxidizing ethyl linoleate and digeranyl at an oxygen pressure of 1 mm. in an attempt to derive  $k_2k_4^{-1}$ . However, serious difficulties were encountered in analyzing the experimental data owing to  $[O_2]$  being appreciably different in the dark and light periods. It was not found possible to make due allowance for this difference at the same time as considering a reaction mechanism involving more than one termination process. The simplifying, but Oxygen absorbed Id time Light Dark FIG. 5.

crude, assumption that the rate-determining propagation step was reaction (2) and that termination occurred solely by reaction (4) under the conditions prevailing was therefore introduced, and it was recognized that the final results could only be roughly quantitative. In this paper, we have adopted the alternative approach, viz., experiments have been restricted to pressure regions where, with high shaking efficiency, it was permissible to neglect the effect on r of changes in  $[O_2]$  during the nonstationary period. Eqn. (13) is only applicable when this assumption is valid. A considerable improvement in precision has thus been effected, but the numerical uncertainty in the derived values still remains rather high. In particular, since measurements do not extend to the pressure region where reaction (4) is the main terminating reaction, our estimates of  $k_2$  and  $k_4$  are only approximate.

<sup>11</sup> See Mayo and Walling, Chem. Rev., 1950, 46, 272; Burnett, Quart. Rev., 1950, 4, 322.



#### Determination of $k_3/k_6$ and $k_2/k_4$

Apparatus.—This is shown in Fig. 6 and was used for all the experiments over the oxygen pressure range covered ( $\sim 5$ -700 mm.). It incorporates several improvements over that used previously: <sup>6</sup> (i) the reaction vessel, glass spiral and manometers were totally immersed in the same thermostat (maintained to  $\pm 0.005^{\circ}$  C); (ii) the spiral was sufficiently flexible to permit a shaking frequency of up to ca. 1000 per min.; (iii) octoil was replaced by lower viscosity silicone fluid in the constant volume manometer and (iv) the shape of the reaction vessel gave improved shaking efficiency, while the wide inset neck prevented small liquid drops momentarily sealing the connecting tube and causing jerky manometer movements. 3 ml. samples of olefin were used. Irradiation was provided by a B.T.H. stabilized 125 W, bare quartz mercury arc, focused on the reaction vessel by a quartz condensing lens through the Pyrex thermostat window. A manually-operated shutter served to interrupt the light. Shaking was effected by a potentiometer-controlled, A.c. stirrer motor, the shaft being rigidly coupled to the stem of the reaction vessel, and was measured to about  $\pm 20$  rev./min. by a Whidbourne stroboscope.



FIG. 6.—A is the pear-shaped reaction vessel ( $\sim 23$  ml.) with glass ring below the neck, B a volume-compensating bulb, C and D, silicone and mercury manometers, respectively. E connects to an electrolytic cell controlled by the make-and-break F. LL indicates the thermostat water level.

The decay and growth intercepts were measured as divisions of a graticule in the cathetometer trained on one limb of the silicone manometer (100 div.  $\simeq 0.4$ mm.). Appropriate calibration to permit these quantities to be expressed in absolute units was effected by directly comparing steady rates of oxidation on the silicone and mercury manometers. Movement of the meniscus over one graticule division corresponded to an oxygen uptake of  $4.20 \times 10^{-6}$  mole  $1.^{-1}$ . Under the best conditions, the intercepts could be defined to  $\pm 0.1$  div.

**Disturbing Factors.**—THE EXPERIMENTALLY OBSERVED INTERCEPTS,  $I_d$  and  $I_g$  are not identical with  $I_d$  and  $I_g$  as defined above, but are equivalently related to them,<sup>6</sup> viz.,

$$I_{d}' = I_{d} + (r_{L} - r_{D})(k_{s}^{-1} + k_{m}^{-1}) \qquad . \qquad . \qquad (14)$$

$$I_{g'} = I_{g} + (r_{L} - r_{D})(k_{s}^{-1} + k_{m}^{-1}), \qquad . \qquad . \qquad (15)$$

where  $k_{\bullet}$  is a constant expressing the shaking efficiency and  $k_{m}$  the speed of manometer response. Since  $k_{m}^{-1}$  was found to be negligible compared with  $k_{\bullet}^{-1}$  in the earlier work <sup>6</sup> and substitution of silicone fluid for octoil ensures more rapid manometer response it need not be further considered.

The term  $(r_L - r_D)k_{\mathfrak{g}^{-1}}$  measures the difference in  $[O_{\mathfrak{g}}]$  produced by changing the reaction rate from  $r_D$  to  $r_L$ , and it is obvious from eqn. (14) and (15) that its effect can in principle be eliminated by using  $(I_{\mathfrak{g}}' - I_{\mathfrak{g}}')$ . It must, however, be stressed that if  $(r_L - r_D)k_{\mathfrak{g}^{-1}}$  is large compared with  $I_{\mathfrak{g}}$  or  $I_{\mathfrak{g}}$ , the experimental uncertainty in the derived constants will necessarily be magnified. Unfortunately, although our investigations have been confined to conditions where  $(r_L - r_D)k_6^{-1}$  is small compared with  $[O_2]$ , it is in most instances large compared with  $I_g$ . Two examples may be quoted from experiments on the oxidation of ethyl linoleate at 550 mm. pressure with a shaking speed of 650 per min. At 15° C,  $I_{a'}$ ,  $I_{g'}$ , and  $(r_L - r_D)k_s^{-1}$  were respectively 27, 19 and 16 (× 10<sup>-6</sup> mole/l.), at 45° C the corresponding figures were 24, 17 and 12. EVALUATION OF  $k_3/k_6$  AND  $k_2/k_4$ .—The non-stationary state data required for solving eqn. (13) for ethyl linoleate and digeranyl\* are presented in Tables II and III, respectively. Also required are values of  $k_3k_6^{-\frac{1}{2}}$ ,  $k_2k_4^{-\frac{1}{2}}$  and  $\phi$  from stationary state measurements: these are given in Table IV. Values of the

TABLE II.— $I_d'$  and  $I_g'$  for Ethyl Linoleate at 25° C Liquid vol., 3 ml.; shaking speed, 650 per min.

PO-	10 <sup>6</sup> /ď	10 <sup>6</sup> <i>I g</i> '	10 <sup>7</sup> 7 L	10 <sup>7</sup> ″D	106a
mm. mole/l		le/1.	/l. mole l.		mole/l.
195	16.0	12.6	22.8	4.74	6·1
31	16.8	12.6	20.9	3.00	5.2
16	15.1	8.4	17.2	3.20	4.3
	13.2	8.4	16.8	1.89	4.9
9.7	9.3	4.5	13.7	1.14	4.0
6.	9.3	4.2	14.0	0.98	3.8
0.0	7.3	2.5	10.0	0.77	3.5
5.4	7.3	1.7	7.8	0.74	2.6
~ T	5.9	1.7	8.8	0.62	2.9

TABLE III.— $I_{d'}$  and  $I_{g'}$  for Digeranyl at 25° C Liquid vol., 3 ml.; shaking speed, 650 per min.

¢0 <sub>2</sub>	10 <sup>6</sup> <i>Id</i> ′	10 <sup>6</sup> <i>I</i> g'	107 <i>r</i> L	1077 <sub>D</sub>	10 <sup>6</sup> a	
mm.	mol	e L-1	mole L	mole 1. <sup>-1</sup>		
711	15.1	8·4 8·4	12.2	1·65 1·72	7.7	
292	19·4 18·5	11·8 11·8	15·9 16·0	2.22	9°1 8·4	
37	14·3 14·3	7·6 8·4	11·0 11·2	1.60 1.61	8·4 7·3	
14	10·5 10·9	4·2 4·2	8.0 9.0	0·95 0·95	6·4 6·5	
7·7 4·9	8·4 13·9	2·5 8·4	6·1 10·4	0.60 1.03	5·3 4·9	

TABLE IV

Olefin	$k_{\rm S}k_6^{-\frac{1}{2}}$ (25°) mole <sup>-\frac{1}{2}</sup> l. <sup>±</sup> sec. <sup>-\frac{1}{2}</sup>	$k_2 k_4^{-\frac{1}{2}}$ (45°) mole $^{-\frac{1}{2}}$ l. $^{\frac{1}{2}}$ sec. $^{-\frac{1}{2}}$	$k_2 k_4 - \frac{1}{2} (25^\circ) *$ mole $-\frac{1}{2} l.\frac{1}{2} \text{ sec.} -\frac{1}{2}$	φ (45°)*
Ethyl linoleate . Digeranyl	$1.21 \times 10^{-2}$ $1.07 \times 10^{-3}$	$\frac{1 \cdot 6 \times 10^3}{0.9 \times 10^3}$	$\begin{array}{c} 2\cdot3\times10^{3}\\ 1\cdot3\times10^{3}\end{array}$	2·5 3·1

\* See text.

\*Since each propagation cycle here results in the incorporation of two molecules of oxygen,4 all velocity coefficients for digeranyl are half those calculated by the equations given.

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last two quantities at 25° have not yet been measured, but adequate correction to the data at 45° is possible; the correction is in fact small and its effect on the values of  $k_2/k_1$  and  $k_3/k_6$  almost negligible. The resulting plots of eqn. (13) show somewhat scattered points (Fig. 7), and statistical regression analyses have therefore been made to ascertain the best linear correlations. These were kindly carried out by Mr. G. E. Blackwell, who reports that highly significant correlation coefficients are found (probability level being better than 0.1%). From the slopes and intercepts of the lines drawn the following results are obtained:



#### Values and Significance of the Velocity Coefficients

The individual k's derived from the measured composite quantities are given in Table V; the uncertainty in the  $k_2/k_4$  and  $k_3/k_6$  values do not justify more than one significant figure being quoted. When compared with earlier results,<sup>6</sup>,<sup>8</sup> considerable discrepancies are apparent, particularly in the absolute values of  $k_3$  and  $k_6$ , and these naturally raise the question of the quantitative significance of such measurements generally. The results now given are believed to be reliable, but we wish to stress most strongly the inherent limitations of the present technique owing to the smallness of the photochemical pre- and aftereffects and the relatively large effects due to delayed oxygen diffusion. It is now clear that at oxygen pressures much below 5 mm. significant

		$\begin{array}{c} 10^6k_2 \\ \times 10^{-6} \end{array}$	k <sub>3</sub> × 10 <sup>−6</sup>	10 <sup>8</sup> k4 × 10 <sup>-6</sup>	10 <sup>6</sup> k <sub>5</sub> × 10 <sup>-6</sup>	10 <sup>5</sup> k <sub>8</sub>
Ethyl linoleate	•	9	бо	20	50	30
Digeranyl		I	3	0·9	9	9

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quantitative estimates are unobtainable, and even at high pressures it is doubtful whether the individual k's are correct to  $\pm$  50 % in the most favourable cases. In less reactive olefins, e.g. methyl oleate and phytene, we know this uncertainty to be increased several fold.

The main conclusion reached previously  $\bullet$  that increased oxidizability (at constant  $r_i$ ) reflects an increase in  $k_3$ , with  $k_6$  remaining substantially constant, is essentially confirmed, although some difference in  $k_6$  appears to be indicated for ethyl linoleate and digeranyl. What is surprising is the higher  $k_4$  value of ethyl linoleate, since energetic considerations require that the reactivity of  $\mathbb{R}^-$  be the inverse of RH, as is indeed consistent with other oxidation features. However, the activation energy of radical-radical interaction is very small and unquestionably steric factors could become dominant and effectively confer special stability on the R-radical from digeranyl.<sup>4</sup>

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