washed neutral with water, then acetone and vacuum dried; yield 3.19 g. The sulfur eliminated as sulfuric acid in the peracetic acid solution corresponded to 2.36% on the weight of I,[14] and the product II contained 1.95% S (total sulfur accounted for 100.2%). The product gave 1.75% S by ion-exchange and 0.087% NH_2, equivalent to 0.174% S. Total sulfonic acid sulfur was thus 1.92% (98.5% of that present). The product dissolved completely in 90% formic acid at 18° in 3 hours, whereas compound I remained insoluble after 10 weeks. It had a considerably increased affinity for the basic dye methylene blue and a marked decrease in affinity for the acid dye Orange II.

The ammonium salt was prepared by adding a few drops of *N* ammonia solution to 1.0 g. of a preparation of N-methylene-66-sulfonic acid (*Anal.* Found: S. 1.99; N, 10.6) and vacuum drying the product.

Anal. Calcd. for ammonium salt: N. 11.5. Found: N, 11.7.

N-Mercaptomethyl-66 Monosulfide (III).—Eight grams of N-mercaptomethyl-66 disulfide (I) (%S 4.30) was allowed to react with 400 ml. of 0.10 *M* potassium cyanide solution at 65° for 6 hours with occasional shaking. The monosulfide was filtered, washed with water, acetone and vacuum dried; yield 7.79 g. *Anal.* Found: S, 2.32. This corresponds to 54.0% of the original sulfur. The solution and washings contained thiocyanate equivalent to 46.5% of the original sulfur.[15] After reaction with cyanide solution for 20 hours, 46.5% of the sulfur was in the product and 53.7% was in solution.

The product III was completely devoid of disulfide sulfur and thiocyanate groups. The latter could not be detected chemically, and the infrared absorption spectrum showed no maximum at 2,000 cm.$^{-1}$ [16] characteristic of the thiocyanate group. The product had the characteristics of a cross-linked polymer in that it remained insoluble in *m*-cresol after 10 weeks. Although N-mercaptomethyl-66 disulfide shows the same insolubility, it dissolves in 24 hours when the disulfide cross-links have been ruptured by reaction with peracetic acid for 24 hours. After reaction of the monosulfide III with peracetic acid, it required 18 days for solution in *m*-cresol.

N-Benzylthiomethyl-66 (V).—N-Mercaptomethyl-66 disulfide (I) was treated with 0.1 *M* hydrochloric acid for 2 hours at 65° and then for 2 hours at 100°.[17] Two grams of I (S 4.16%) was warmed with a solution of 9.2 g. of thioglycolic acid and 11.2 g. of potassium hydroxide in 100 ml. of 80% methanol. After cooling to room temperature, 16.5 g. of benzyl chloride was added with cooling and the mixture was allowed to stand overnight; 200 ml. of water was then added when the original small precipitate dissolved and a fine white granular precipitate was obtained. The N-benzylthiomethyl-66 was filtered, washed with water, dilute ammonia and ether and vacuum dried; yield 2.04 g. *Anal.* Found: S, 3.82; disulfide S, 0.09. Calcd. for $-S-S \rightarrow 2-SCH_2.C_6H_5$: S, 3.72. Compound V showed infrared absorption maxima at 699 and 768 cm.$^{-1}$ (monosubstituted benzene derivative) and was readily soluble in formic acid and warm 80% methanol.

N-Benzylthiomethyl-66 Sulfone (VI).—N-Benzylthiomethyl-66 (S 3.82%, 1.0 gram) was allowed to react with 25 ml. of 2% aqueous peracetic acid solution for 24 hours at 18°, with occasional shaking. The oxygen take-up was 2.01 atoms per atom of sulfur. The sulfone VI was filtered off, washed with water and vacuum dried. Compound VI showed infrared absorption maxima at 1,119 and 1,323 cm.$^{-1}$ ($<SO_2$), in addition to those at 698 and 769 cm.$^{-1}$.

Anal. Calcd. for $-SCH_2C_6H_5 \rightarrow -SO_2.CH_2C_6H_5$: S, 3.58. Found: S, 3.64.

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[14] After 24, 48, 96 and 192 hours reaction with peracetic acid, 53.7, 54.8, 54.4 and 53.3%, respectively, of sulfur was removed from the disulfide as sulfuric acid, showing that equation b represents a terminal reaction.

[15] W. W. Scott and N. H. Furman, "Standard Methods of Chemical Analysis," Lancaster Press, Inc., Lancaster, Pa., 1952, p. 277.

[16] Determined on a Grubb–Parsons double-beam spectrometer, using the potassium bromide disk technique. See M. M. Stimson and M. J. O'Donnell, THIS JOURNAL, **74**, 1805 (1952).

[17] This was to remove methoxymethyl groups, which show an infrared absorption peak at 1080 cm.$^{-1}$, and may be confused with one of the sulfone peaks. The removal of these groups is not essential for the preparation.

BRADFORD, ENGLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Diacyl Peroxides. III.[1] The Reaction of Phthaloyl Peroxide with Olefins

BY FREDERICK D. GREENE AND WILLIAM W. REES

RECEIVED DECEMBER 18, 1957

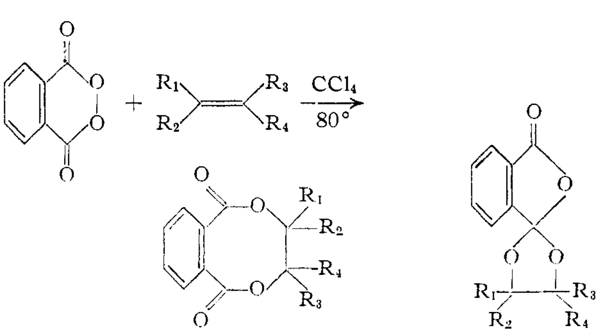
Oxidation of olefins by phthaloyl peroxide has been shown to be general and to obey second-order kinetics. With olefins lacking allylic hydrogen, mixtures of cyclic phthalate (I) and lactonic *ortho*-ester (II) are obtained. Involvement of the allylic position is observed with olefins such as cyclohexene in which 2-cyclohexenyl hydrogen phthalate is a major product (45% yield) of the reaction. A kinetic study has revealed a marked similarity of phthaloyl peroxide to peracetic acid, dibromocarbene and bromine in relative reactivity toward aliphatic olefins, and a reaction constant, rho, of −1.65 for reaction of phthaloyl peroxide with substituted *trans*-stilbenes. Preference is indicated for a mechanism involving bimolecular reaction of neutral peroxide and olefin rather than attack on olefin by diradical derived from oxygen–oxygen fission.

Comparison of the cyclic diacyl peroxide, monomeric phthaloyl peroxide, with acyclic analogs has revealed marked differences in behavior.[1-3] Of particular interest is the behavior toward olefins. Phthaloyl peroxide has been shown to undergo a stereospecific addition reaction with *cis*- and *trans*-stilbene.[1]

In the present paper, the reaction of phthaloyl peroxide with a series of olefins is considered in detail.

Results

Kinetics.—Phthaloyl peroxide reacts with olefins in carbon tetrachloride in a process that is first



	I	II
$R_1 = R_3 = C_6H_5$ $R_2 = R_4 = H$	40%	60%
$R_1 = R_4 = C_6H_5$ $R_2 = R_3 = H$	25%	75%

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[1] Part II, F. D. Greene, THIS JOURNAL, **78**, 2250 (1956).

[2] K. E. Russell, *ibid.*, **77**, 4814 (1955).

[3] F. D. Greene, *ibid.*, **78**, 2246 (1956).

order in olefin and first order in peroxide. The data for a number of aliphatic and phenyl-substituted olefins are summarized in Table I. Examination shows a fifteen hundred-fold range in rate between 1-methylcyclopentene and 1-decene.

TABLE I

REACTION OF PHTHALOYL PEROXIDE WITH OLEFINS IN CARBON TETRACHLORIDE

Olefin	Temp., °C.	$k_2 \times 10^3$, M^{-1} sec.$^{-1}$
1-Methylcyclopentene	80	214
Trimethylethylene	80	67[a]
	23	1.28
1,1-Diphenylpropene-1	80	54.4
	45	6.13
	23	1.07
Indene	80	50[b,c]
Triphenylethylene	80	31.9
1,1-Diphenylethylene	80	15.9
trans-Stilbene	80	13.7
cis-Stilbene	80	7.18
Cyclohexene	80	6.83
Tetraphenylethylene	80	6.5[a]
	45	0.60[a]
Styrene	80	1.77
1-Decene	80	0.14
Allylbenzene	80	0.11[c]

[a] Initial rate. [b] See Experimental section. [c] Approx.

In Table II are summarized the data for a series of monosubstituted *trans*-stilbenes, showing a six hundred forty-fold range in rate between *p*-methoxy- and *p*-nitro-*trans*-stilbene.

TABLE II

REACTION OF PHTHALOYL PEROXIDE WITH MONOSUBSTITUTED *trans*-STILBENES IN CARBON TETRACHLORIDE

Substituent	Temp., °C.	$k_2 \times 10^3$, M^{-1} sec.$^{-1}$	$\sigma +$ [a]
p-OCH_3	23	18.8	−0.764
	45	78.7	
	80	(532.0)[b]	
p-CH_3	80	43.7	− .306
H	80	13.7	.000
p-Cl	80	9.08	.112
m-Cl	80	3.44	.373
p-$COOCH_2CH_3$	80	3.50	.473[c]
p-NO_2	80	0.74	.777

[a] Ref. 14. [b] Calcd. from data at 23 and 45°. [c] H. C. Brown, Abstracts of the Fifteenth National Organic Chemistry Symposium, Rochester, N. Y., June 17–20, 1957, p. 60.

The reactions of Tables I and II showed adherence to second-order kinetics throughout the range studied, 0–85%, with the exceptions of trimethyl- and tetraphenylethylene. In both of these cases calculated second-order rate constants increased toward the end of reaction.

Products.—The products of reaction of phthaloyl peroxide with olefins are dependent on the nature of the olefin. The principal difference is associated with the presence or absence of hydrogen in the allylic position. The nature of the reaction of phthaloyl peroxide with the substituted stilbenes was ascertained from two compounds which were considered representative, the *p*-methoxy and the *m*-chloro derivatives. Both product mixtures consisted of cyclic phthalate I and lactonic *o*-ester II in which the latter compound predominated, determined by infrared analysis of the mixtures utilizing the 1775 cm.$^{-1}$ band for lactonic *o*-ester and the 1730 and 1100 cm.$^{-1}$ bands for cyclic phthalate. The infrared absorption spectra of the product mixtures were remarkably close to that obtained with *trans*-stilbene.[1] Substitution in the *m*- or *p*-position appears to have very little effect on the ratio of the two products I and II, but as noted above has an appreciable effect on rate.

Spectroscopic examination of the products derived from the phenyl-substituted ethylenes revealed an increase in the ratio of lactonic *o*-ester to cyclic phthalate with increasing phenylation of the ethylene. The infrared spectrum of the crude product derived from tetraphenylethylene has strong absorption at 1780 cm.$^{-1}$ (II) and negligible absorption at 1730 cm.$^{-1}$ (I).

The nature of the reaction of phthaloyl peroxide with olefins possessing hydrogen in an allylic position was examined in detail in the case of cyclohexene. The major product of this reaction was the half-acid ester of cyclohexenol and phthalic acid, 2-cyclohexenyl hydrogen phthalate, isolated in 45% yield. This compound was characterized by identity of infrared absorption spectrum with an authentic sample prepared by standard methods. Further confirmation was obtained by conversion of both samples to the corresponding benzylammonium salts, identical in infrared absorption spectra and showing no m.p. depression. From the balance of the products was isolated phthalic anhydride (14% yield) and a neutral fraction (40% yield) consisting largely of cyclic phthalate and lactonic *o*-ester. Hydrolysis of this fraction afforded *cis*-1,2-cyclohexanediol, of identical infrared spectrum and showing no m.p. depression with an authentic sample, and phthalic acid, characterized as the anhydride.

Both direct and indirect paths are available, *a priori*, for the formation of half-acid ester and phthalic anhydride. Indirect routes have been rendered unlikely by demonstrations of the stability of the products under the reaction conditions. Subjection of a sample of 2-cyclohexenyl hydrogen phthalate to refluxing carbon tetrachloride for one day led to recovery of half-acid ester uncontaminated by phthalic anhydride. The cyclic phthalate (or lactonic *o*-ester) has been shown not to be the precursor of the half-acid ester (*e.g.*, *via* an elimination-type reaction) in that subjection of a solution of phthaloyl peroxide and cyclohexene in carbon tetrachloride at 80° to a ninefold increase in reaction period effected only a slight change in product composition. The change noted was a slight increase in the amount of phthalic anhydride accompanied by a slight decrease in the amount of half-acid ester. This is consistent with the slow decomposition of *cis*- and *trans*-5-methyl-2-cyclohexenyl hydrogen phthalate in acetonitrile at elevated temperature to 5-methyl-1,3-cyclohexadiene and phthalic anhydride.[4] The oxidation product of the process in which phthaloyl peroxide is reduced to phthalic anhydride is not known. It is presumed to be cyclohexenol or cyclohexene oxide. The

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(4) H. L. Goering, D. P. Blanchard and E. F. Silversmith, THIS JOURNAL, **76**, 5409 (1954).

presence of hydroxyl absorption in the infrared absorption spectrum of the original product mixture favors the former possibility.

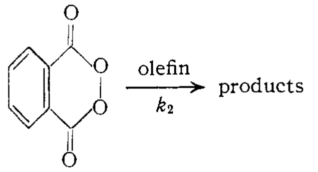
The characteristic bands in the infrared absorption spectrum of the half-acid ester (2700-2500, 1740-1700, 1300-1275 cm.$^{-1}$) are observed in the crude product mixtures derived from 1-methylcyclopentene, trimethylethylene and α-methylstyrene, a finding that is strongly suggestive of the general involvement of allylic hydrogen in the oxidation by phthaloyl peroxide of olefins possessing this structural feature. An important exception to this generalization is the reaction of 1,1-diphenylpropene-1 with phthaloyl peroxide, in which the product mixture possesses strong absorption in the infrared at 1775 cm.$^{-1}$ (lactonic *o*-ester), weak absorption at 1730 cm.$^{-1}$ (cyclic phthalate), and the complete absence of the bands characteristic for half-acid ester.

Effect of Temperature.—Activation parameters have been determined for the reaction of phthaloyl peroxide with 1,1-diphenylpropene-1, with *trans-p*-methoxystilbene and with tetraphenylethylene. The rate of reaction of the first one at three temperatures shows adherence to the Arrhenius equation and activation parameters of $\Delta H^{\ddagger}$, 13.3 kcal./mole; $\Delta S^{\ddagger}$, -27.1 e.u. The activation parameters for *trans-p*-methoxystilbene are $\Delta H^{\ddagger}$, 11.6 kcal./mole; $\Delta S^{\ddagger}$, -27.3 e.u. (The corresponding parameters for the reaction of perbenzoic acid with *trans-p*-methoxystilbene in benzene at 30° are $\Delta H^{\ddagger}$, 14.5 kcal./mole; $\Delta S^{\ddagger}$, -22.3 e.u.[5]). For tetraphenylethylene, activation parameters based on the initial second-order rate constants are $\Delta H^{\ddagger}$, 14.6 kcal./mole; $\Delta S^{\ddagger}$, -27.6 e.u., indicating that the enthalpy of activation is largely responsible for the decrease in rate for this olefin. The large negative values for the entropy of activation are in accord with expectations for bimolecular reactions of this type.

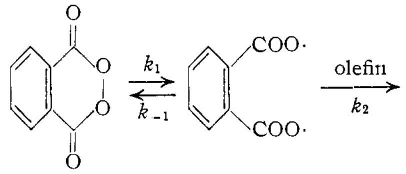
The infrared absorption spectra of the product mixtures derived from the reaction of phthaloyl peroxide with 1,1-diphenyl-1-propene at 23° and at 80° were practically identical, indicating a close correspondence in activation parameters for the processes giving rise to the product mixture.

Discussion

The reaction of phthaloyl peroxide with olefins has been amenable to study because of the marked stability of the peroxide alone in carbon tetrachloride at elevated temperatures (50% destruction of a solution initially 0.01 *M* in peroxide requires 15 days at 80°). This stability may be a property of this ring system or may be due to facile ring closure following homolytic fission of the oxygen–oxygen bond.[6] In view of these possibilities, two principal mechanistic paths, 1 and 2, for the olefin reaction warrant consideration.[1]



(1)

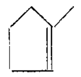
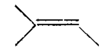
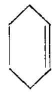


(2)

The nature of the reaction of phthaloyl peroxide with olefins is revealed by examination of the effects of changes in olefin structure on reactivity shown in Tables I and II, and comparison of the behavior of phthaloyl peroxide with other reagents capable of undergoing reaction with unsaturated compounds. In Table III are summarized relative rates of attack of phthaloyl peroxide, peracetic acid,[7] dibromocarbene,[8] bromine[9] and trichloromethyl radical[8] on a series of aliphatic olefins. The correspondence in relative rates for phthaloyl peroxide with those for the "double bond reagents," peracetic acid, dibromocarbene and bromine (as far as the data are available) is striking. The relationship of olefin structure to peracid attack has been discussed in detail by Swern.[7] Attachment of electron-releasing groups to an ethylene unit leads to increased rate of reaction. Phthaloyl peroxide is seen to be most discriminating of the electrophilic reagents listed in Table III.

TABLE III

COMPARISON OF RELATIVE REACTIVITY OF OLEFINS WITH VARIOUS REAGENTS

Olefin	Phthaloyl peroxide[a]	Peracetic acid[b]	Dibromocarbene[c]	Bromine[d]	Trichloromethyl radical[e]
	31.3	17.2			
	9.37	9.61	8.0	1.04	3.8
	1.00	1.00	1.00		1.00
C_6H_5— 	0.259	0.087	1.0	0.34	420
Alkyl— 	0.021	0.037	0.18	0.20	4.2
Benzyl— 	0.016	0.015	0.05		2.9

[a] See Table I. [b] By rate measurement in acetic acid, 25°, ref. 7. [c] By competition experiments in *t*-butyl alcohol–pentane, 0°, ref. 8. [d] By competition experiments in methylene chloride, −78°, ref. 9. [e] By competition experiments, see ref. 11, p. 254.

The first four reagents of Table III, of marked similarity in rate pattern toward olefins, also have the common feature of stereospecificity in reaction.[1,7,8,10] In both of these respects, trichloromethyl radical attack on olefins stands in great contrast.[8,11] The divergence in behavior between trichloromethyl radical and dibromocarbene has

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(5) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(6) It is hoped that experiments in progress on the O^{18} peroxide may bear directly on this question.

(7) D. Swern, THIS JOURNAL, **69**, 1692 (1947).

(8) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(9) S. V. Anantakrishnan and R. Venkataraman, *Chem. Revs.*, **33**, 27 (1943).

(10) W. von E. Doering and P. LaFlamme, THIS JOURNAL, **78**, 5447 (1956).

(11) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 254, 266.

been cited as evidence for the direct addition of the latter to the double bond rather than stepwise addition *via* a diradical intermediate[8]; application of this argument to the case of phthaloyl peroxide would favor path 1 over path 2. However, if dibromocarbene and phthaloyl peroxide were to add as radicals, they could be expected to act as strongly electron-accepting radicals. The validity of that part of the above argument which is based on relative reactivity then rests on the assumption that the trichloromethyl radical is equally electron-accepting. The evidence on this point is conflicting.[12] In the absence of data for attack on a series of simple olefins by a strongly electron-accepting radical, the possibility that the relative rate data for such a case might follow the pattern observed in olefin attack by reagents such as peracids cannot be excluded with rigor. In support of Skell's argument is the observation that the electron-accepting thiyl radical from *n*-butyl mercaptan shows the same preference for styrene over a terminal olefin, 1-pentene, (100 to 1)[13] that is shown by the trichloromethyl radical.

Further support for the electrophilic nature of the attack of phthaloyl peroxide on olefins is found in the data on the substituted *trans*-stilbenes. These data and comparable data for perbenzoic acid[5] are illustrated in Fig. 1. Two points are of special interest. First, the reaction constant, ρ, for reaction with phthaloyl peroxide is -1.65 and for reaction with perbenzoic acid is -1.02. Secondly, the plots of log relative rates *vs.* σ^+ afford an excellent correlation for both series (plots *vs.* σ are less satisfactory showing strong upward curvature in the region of electron-donating substituents). The negative values of ρ indicate that both reagents are electrophilic, and the greater value of ρ for phthaloyl peroxide characterizes this reagent as the more electron-demanding of the two. The σ^+ substituent constants, developed for aromatic substitution, have been shown to be of value in correlating both the nuclear and side chain electrophilic reactions of aromatic systems.[14]

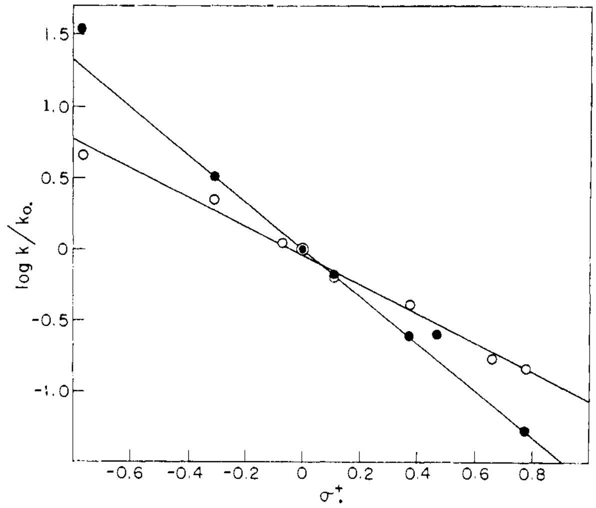

Fig. 1.—Reaction of substituted *trans*-stilbenes with phthaloyl peroxide in carbon tetrachloride at 80° (●) and with perbenzoic acid in benzene at 30° (○).

TABLE IV

DATA FOR PHENYL-SUBSTITUTED ETHYLENES

Olefin	Phthaloyl peroxide, rel. k_2[a]	Perbenzoic acid,[b] rel. k_2	"Methyl affinity"[c]
Styrene	0.259	1.10	1630
1,1-Diphenylethylene	2.33	3.70	
cis-Stilbene	1.05	1.01	
trans-Stilbene	2.00	0.52	183
Triphenylethylene	4.67	.24	85
Tetraphenylethylene	0.95	.022	<25

[a] Same scale as in Table III. [b] Ref. 5. [c] Ref. 15.

A third comparison of phthaloyl peroxide with peracid is given in Table IV, in which the previously close correspondence between these two reagents breaks down. Increasing phenylation of ethylene results in decreasing ease of attack by perbenzoic acid, $k_{\text{styrene}}/k_{\text{tetraphenylethylene}} = 50$. With phthaloyl peroxide an increase in rate is noted for increasing phenylation up to triphenylethylene, $k_{\text{triphenylethylene}}/k_{\text{styrene}} = 18$, followed by a decrease for tetraphenylethylene, $k_{\text{tetraphenylethylene}}/k_{\text{triphenylethylene}} = 0.19$. (This general pattern is already reflected in Table III by the larger ratio of attack on styrene relative to 1-decene for phthaloyl peroxide than for peracetic acid.) The decreasing ease of attack by perbenzoic acid with increasing degree of phenylation of ethylene is accompanied by an increase in both the enthalpy and entropy of activation, and indeed shows a good correlation with the bond localization energies of the double bonds.[5] The difference in the relative rate pattern for phthaloyl peroxide is not inconsistent with consideration of phthaloyl peroxide as the more electron-demanding reagent of the two: the reagent of greater electron demand calling forth the greater response from the phenyl groups attached to the ethylene unit. Table IV also includes data on "methyl affinities" (rate of reaction of methyl radical with substrate relative to benzene).[15] With the reservations noted before in the discussion of the trichloromethyl radical, the opposing behavior of the methyl radical and phthaloyl peroxide may be construed as evidence against a mechanism involving addition of diradical III to olefin in a stepwise fashion. This series of olefins may be of use in distinguishing the modes of reaction of "double bond reagents" (*e.g.*, osmium tetroxide, ozone and the reagents of Table III) with olefins.

Any mechanism for the reaction of phthaloyl peroxide with olefins must take into consideration the following experimental facts: (1) rate of reaction with olefins is second order, (2) the reaction is highly stereospecific with olefins lacking allylic hydrogen[1] and (3) electron accession to the olefinic link results in increased rate of reaction. The simplest representation of the reaction that embraces these facts is association of phthaloyl peroxide with the double bond, involving partial charge transfer from the π-electron cloud to the peroxide moiety,

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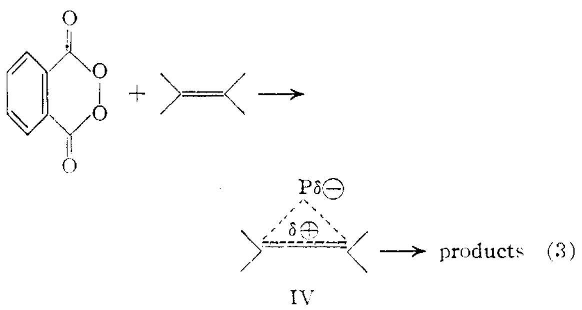
(12) See ref. 11, pp. 158, 255, 265; E. C. Kooyman, R. Van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **B56**, 75 (1953); R. L. Huang, *J. Chem. Soc.*, 1749 (1956).

(13) See ref. 11, p. 322.

(14) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

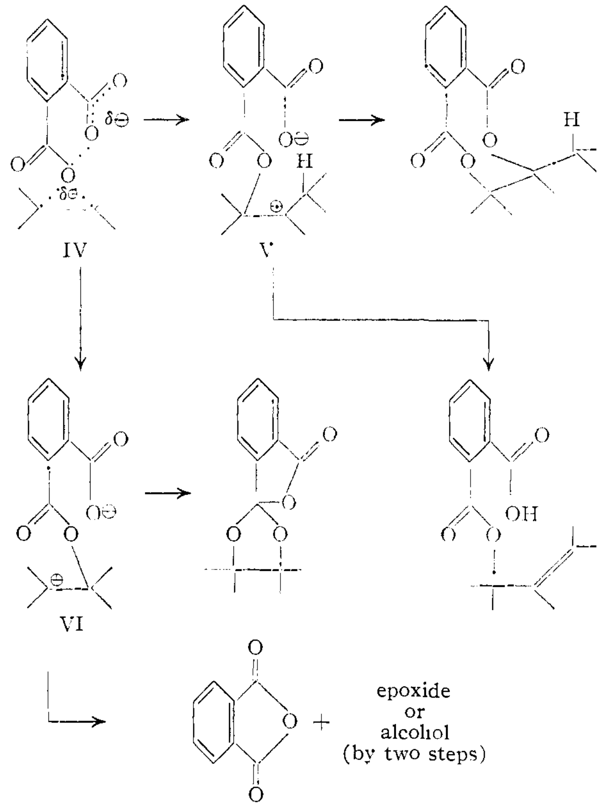
(15) M. Szwarc and F. Leavitt, THIS JOURNAL, **78**, 3590 (1956).

followed by conversion of the complex to products.

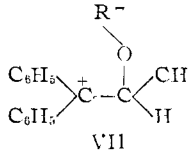


The observed diversity of products may be explained by partition of complex IV to "ion pairs" V and VI (written with full charge separation for simplicity in representation) followed by conversion of V and VI to products, as indicated in Chart I.

CHART I

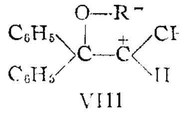


For reaction of phthaloyl peroxide with unsymmetrical olefins one might expect, by this ionic representation, preferential conversion of complex IV to that ion pair which affords the greater delocalization of positive charge. In the case of 1,1-diphenylpropene-1, this argument suggests that "ion pairs" of type VII (positive charge at the benzhydryl carbon atom) will take preference over those of type VIII (positive charge at the secondary carbon atom).



$(C_6H_5)_2\overset{+}{C}-CH(CH_3)-O-R^-$

VII



$(C_6H_5)_2C(O-R^-)-\overset{+}{C}H(CH_3)$

VIII

The lack of involvement of allylic hydrogen in the reaction of phthaloyl peroxide with 1,1-diphenylpropene-1 is consistent with this view in that the path by which half-acid ester formation is represented in Chart I is not available to VII. Instead, the only products from this olefin are lactonic *o*-ester and cyclic phthalate.

The close similarity of product composition in reaction of phthaloyl peroxide and 1,1-diphenylpropene-1 at 23 and at 80° is suggestive of the intervention of an intermediate in that a scheme employing several independent routes from reactants to products would require the unlikely situation of the conversion of one pair of reactants to two markedly different products with essentially identical activation parameters for the two processes. The closeness in rate constant for 1,1-diphenylethylene and *trans*-stilbene suggests that an oxygen atom of phthaloyl peroxide has not been firmly committed to a particular carbon atom of the carbon–carbon double bond at the transition state.

In view of the importance of polar effects in many free radical reactions,[16] the characterization of the attack of phthaloyl peroxide on olefins as electrophilic in nature does not exclude the diradical mechanism (equation 2), but this process is considered less likely than the direct possibilities for the reasons given earlier.

Experimental[17]

Phthaloyl peroxide was prepared by the methods described previously.[2,3] Material of at least 97% purity, obtained by recrystallization from methylene chloride, was used in all kinetic experiments.

Preparation of Olefins.—The kinetic experiments were performed with olefins obtained from commercial sources or prepared by standard methods of the following physical constants: cyclohexene, b.p. 82–83°, n^{20}_{D} 1.4461 (reported[18] b.p. 83°, n^{20}_{D} 1.4465); styrene, twice distilled under nitrogen at reduced pressure, n^{20}_{D} 1.5457 (reported[18] n^{20}_{D} 1.5468); 1-decene, b.p. 169–170°, n^{20}_{D} 1.4216 (reported[19] b.p. 171°, n^{20}_{D} 1.4217); trimethylethylene, b.p. 38°, n^{30}_{D} 1.3813 (reported[19] b.p. 38.4°, n^{30}_{D} 1.3814); indene (tech., redistilled), b.p. 90° at 52 mm., n^{20}_{D} 1.5721 (reported[20] b.p. 114° at 100 mm., n^{20}_{D} 1.5764); 1-methylcyclopentene (prepared by dehydration of a commercial sample of 1-methylcyclopentanol), b.p. 75–76°, n^{20}_{D} 1.4326 (reported[18] b.p. 75.8°, n^{20}_{D} 1.4330); allylbenzene (vapor phase chromatogram yielded a single, well-defined peak) was prepared from allyl bromide and phenylmagnesium bromide,[21] b.p. 156–157°, n^{29}_{D} 1.5068 (reported[19] b.p. 156.3°, n^{20}_{D} 1.5118); triphenylethylene, m.p. 68–69° (reported[19] m.p. 70°); 1,1-diphenylethylene, b.p. 144–145° at 13 mm., n^{20}_{D} 1.6069 (reported[22] b.p. 148° at 15 mm., n^{20}_{D} 1.6075); 1,1-diphenyl-1-propene, m.p. 49.5–50° (reported[19] m.p. 51°); tetraphenylethylene, m.p. 225–226° (reported[10] m.p. 222°); *trans*-stilbene, m.p. 123–124° (reported[19] m.p. 124°); 4-chlorostilbene, furnished by Professor H. O. House, m.p. 130–131° (reported[5] m.p. 130°); 4-carbomethoxystilbene, prepared by the method of Fuson and Cooke[23] was converted to 4-carbethoxystilbene by hydrolysis and re-esterification, m.p. 103–104° (reported[23] m.p. 105–106°); samples of 4-methoxystilbene, m.p. 135.5–136.5° (reported[5] m.p. 135°); 4-methylstilbene, m.p. 119–

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(16) See ref. 11, pp. 132–140, 628, for leading references.

(17) Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

(18) "Physical Properties of Chemical Compounds," American Chemical Society, Washington, D. C., 1955.

(19) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1946, Vols. I–III.

(20) G. A. Russell, THIS JOURNAL, **78**, 1035 (1956).

(21) E. B. Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).

(22) R. H. Shapiro, R. P. Linstead and D. M. Newitt, *J. Chem. Soc.*, 1784 (1937).

(23) R. C. Fuson and H. G. Cooke, Jr., THIS JOURNAL, **62**, 1180 (1940).

119.7° (reported[5] m.p. 118°); 4-nitrostilbene, m.p. 154–155° (reported[5] m.p. 155°); and 3-chlorostilbene, m.p. 75–76° (reported[24] m.p. 73–74°) were prepared by the general method of Meerwein.[25]

Kinetic Method.—The rate of reaction of peroxide with the olefins was followed by titrimetric analysis for peroxide by the method described previously.[1] Spectrophotometric analysis of the rate of change in ultraviolet absorption spectrum was used with 1-methylcyclopentene. All reactions of Tables I and II except for the three designated in Table I showed adherence to second-order kinetics throughout the range studied (0–85% reaction). The average deviation within a run was usually 2–3%. An illustrative run is shown in Table V.

TABLE V

RATE OF REACTION OF 4-METHOXYSTILBENE[a] WITH PHTHALOYL PEROXIDE[a] IN CARBON TETRACHLORIDE AT 23°

Time, sec. × 10^{-3}	Thiosulfate[b] soln., ml.	$k_2 \times 10^3$ l. mole^{-1} sec.$^{-1}$
0	12.20	
0.49	11.11	18.5
1.29	9.71	18.5
2.21	8.47	18.4
3.61	6.97	19.3
5.36	5.82	18.9
7.72	4.73	19.0
10.17	3.96	18.9
15.10	2.98	18.9
	Av. k_2	18.8 ± 0.3

[a] Initial concentrations, 0.0108 *M*. [b] 0.00885 *N*.

2-Cyclohexenyl Hydrogen Phthalate.—A sample of 2-cyclohexenol, prepared by hydrolysis[26] of 3-bromocyclohexene,[27] was converted to the half-acid phthalate by a standard method.[28] The product was recrystallized two times from ether–petroleum ether, colorless prisms, m.p. 64.5–65.5°.

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.29; H, 5.73. Found: C, 68.36; H, 5.87.

The half-acid phthalate was converted to the salt, 2-cyclohexenyl benzylammonium phthalate, by the general method of Buehler, Carson and Edds.[29] The salt was obtained in 86% yield in the form of small colorless needles. Recrystallization from ethyl acetate afforded material of m.p. 132–134°.

Anal. Calcd. for $C_{21}H_{23}NO_4$: C, 71.34; H, 6.56; N, 3.96. Found: C, 71.47; H, 6.53; N, 3.98.

Reaction of Phthaloyl Peroxide with Cyclohexene—A solution of 0.97 g. (5.92 mmoles) of phthaloyl peroxide and 6.2 g. (75.6 mmoles) of cyclohexene in 100 ml. of reagent carbon tetrachloride was heated at reflux for 16 hr. The solvent and excess olefin were removed under reduced pressure. The infrared spectrum showed absorption at 3500 (shoulder), 3300–2500(broad), 1855, 1797, 1780 and 1740–1720 cm.$^{-1}$ indicative of the presence of half-acid phthalate, anhydride and lactonic *o*-ester (cyclic phthalate band is obscured by the half-acid ester). The colorless semi-solid residue was dissolved in ether and extracted with 60 ml. of 5% sodium bicarbonate solution. The ether layer was dried over magnesium sulfate. The aqueous alkaline layer was washed with chloroform and acidified with 5% hydrochloric acid. The acid was extracted with chloroform and dried over calcium chloride. Removal of solvent afforded 0.65 g. (45% yield) of colorless oil, identical in infrared absorption spectrum with authentic 2-cyclohexenyl hydrogen phthalate. A sample of the acidic oil was converted in high yield to the benzylammonium salt as indicated above, affording material of m.p. 132–133° after one recrystallization from ethyl acetate, shown to be 2-cyclohexenyl benzylammonium phthalate by identity in infrared absorption spectra and mixed m.p. of 133–134°.

The ether solution containing the neutral products of reaction was dried over magnesium sulfate, filtered and solvent was removed. The infrared spectrum of the residue showed strong absorption at 1725–1720 and 1100 cm.$^{-1}$ (cyclic phthalate I), at 1780 cm.$^{-1}$ (lactonic *o*-ester II), and at 1795 and 1855 cm.$^{-1}$ (phthalic anhydride). The residue was recrystallized from carbon tetrachloride yielding 0.12 g. (14% yield) of white needles, m.p. 124–130°. Sublimation and recrystallization from benzene–petroleum ether afforded 0.09 g. of pure phthalic anhydride, m.p. 129–131°, mixed m.p. with an authentic sample, 129.5–131.5°.

Concentration of the carbon tetrachloride filtrate afforded 0.76 g. of oil which was heated in 25 ml. of 75% aqueous ethanol containing 4 g. of sodium hydroxide for 19 hr. The resulting dark solution was diluted with 200 ml. of water and continuously extracted with ether for 24 hr. Acidification of the aqueous phase, extraction with ethyl acetate, removal of solvent after drying over magnesium sulfate and trituration of the residue with chloroform afforded 0.22 g. (22%) of crude phthalic acid, dec. p. 183–185°, identified by sublimation to phthalic anhydride, m.p. 129–131°, mixed m.p. 129–131°.

Concentration of the ether phase from the continuous extraction afforded 0.34 g. of viscous dark oil which was chromatographed on 10 g. of basic alumina. Elution with ether–methanol (4:1) afforded 0.094 g. of crude *cis*-1,2-cyclohexanediol, m.p. 64–73°, at least 67% *cis*-diol by infrared analysis. Three recrystallizations from ethyl acetate–petroleum ether yielded pure *cis*-1,2-cyclohexanediol, m.p. 95–98°, identical in infrared absorption spectrum with an authentic sample, mixed m.p. 98–99°.

Stability of Products to Conditions of Formation.—A solution of phthaloyl peroxide and cyclohexene in carbon tetrachloride was heated in a sealed tube for 140 hr. at 80°. The infrared absorption spectrum of the crude product mixture was similar to that obtained from a 16-hr. run but revealed a small increase in phthalic anhydride and a small decrease in 2-cyclohexenyl hydrogen phthalate. Subjection of a 0.17-g. sample of pure 2-cyclohexenyl hydrogen phthalate to a 24-hr. reflux period in carbon tetrachloride, and recovery afforded material of identical infrared absorption spectrum with starting material.

Reaction of Phthaloyl Peroxide. (a) **With *p*-Methoxy- and *m*-Chlorostilbene.**—Equivalent amounts of peroxide and olefin were allowed to react to completion in carbon tetrachloride at 80°. Removal of solvent and inspection of the infrared absorption spectra of the crude residues in chloroform solution showed strong absorption at 1770 cm.$^{-1}$ (lactonic *o*-ester, II) and at 1730, 1100 cm.$^{-1}$ (cyclic phthalate I). The relative intensities of the 1770 and 1730 cm.$^{-1}$ bands were approximately the same for the two product mixtures.

(b) **With 1,1-Diphenylpropene-1.**—A solution of peroxide and olefin in carbon tetrachloride, 0.004 *M* in each reactant, was divided in two parts; one part was heated at 80°, the other was allowed to run to completion at 23°. The infrared absorption spectra of both mixtures were practically identical, exhibiting strong absorption at 1775 cm.$^{-1}$ (lactonic *o*-ester), weak absorption at 1725 cm.$^{-1}$ (cyclic phthalate) and the complete absence of absorption characteristic of half-acid phthalate.

(c) **With α-Methylstyrene.**—Equivalent amounts of olefin and peroxide in carbon tetrachloride were allowed to react to completion at 80°. The infrared absorption spectrum of the crude product mixture possessed a sharp band at 1775 cm.$^{-1}$ (lactonic *o*-ester), bands at 1795 and 1855 cm.$^{-1}$ (phthalic anhydride) and broad absorption at 2700–2500, 1740–1660 cm.$^{-1}$ (half-acid ester).

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[24] F. Bergmann, J. Weizmann and D. Schapiro, *J. Org. Chem.*, **9**, 408 (1944).

[25] H. Meerwein, E. Buchner and K. van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

[26] A. Berlande, *Bull. soc. chim. France*, **9**, 644 (1942).

[27] K. Ziegler, A. Späth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

[28] H. W. Hills, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 576 (1936).

[29] C. A. Buehler, L. Carson and R. Edds, THIS JOURNAL, **57**, 2181 (1935).