boiling water for 2 days. The aqueous solution was evaporated to dryness several times with the aid of a water-bath and an aspirator until there was obtained a negative test for chloride ion. The chloride-free acid was neutralized with lithium carbonate, and the salt was crystallized from hot ethanol–acetone as fine needles. In this solvent, the salt was more soluble at room temperature than at higher temperatures. The salt tested chloride-free and its acetic acid solution gave no test for acid or base and gave zero water titer by Karl Fischer titration.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Influence of Polar Substituents and Polar Solvents on Radical Decomposition Reactions[1]

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The radical decomposition of dibenzoyl diimides and dibenzoyl peroxides is subject to polar substituent, solvent and catalytic effects resembling those observed in non-radical reactions.

Introduction

If it is assumed that the transition state and products of a radical dissociation reaction are very much like the original molecule in their charge distribution, then purely polar effects on radical dissociation rates and equilibria should be correspondingly small. Such reactions should be relatively unresponsive to substituents or at least should give a response not well correlated with that of well known heterolytic reactions. They should also be unresponsive to the polar nature of the solvent or to the addition of acidic or ionic catalysts.

If on the other hand a considerable change in charge distribution occurs during a radical decomposition reaction, then such a reaction can be expected to resemble heterolytic reactions to a considerable degree. Examples are the correlation of the rates of some undoubtedly radical dissociation reactions by means of the Hammett equation,[3] the stabilization of diradicals by acids and by Lewis acids,[4] and the well-known stability of semiquinone radicals and their nitrogen analogs in basic and acidic media, respectively.[5]

The interpretation of the rate of radical dissociation reactions is particularly difficult because of the common occurrence of radical chain transfer to the solvent. A faster decomposition in a given solvent may be the result of an acceleration of the initial decomposition or of the decomposition induced by the especially reactive radicals derived from that solvent, essentially a structural rather than a medium effect. Fast radical decompositions in polar solvents have usually been interpreted in the latter way rather than as acceleration of the initial decomposition reaction, even when no chain inhibitor is known which will reduce the rate to that in a slow solvent.

The Decomposition of Dibenzoyl Diimides

The decomposition of dibenzoyl diimide responds to polar substituents, to nucleophilic solvents and to acid catalysts and the response is, in the authors' opinion, an acceleration of the radical reaction rather than a shift to a faster heterolytic mechanism. However, it is still uncertain to what extent the nucleophilic solvents accelerate the initial radical decomposition and to what extent they merely provide better radicals for the chain decomposition. The decomposition products of the diimides are complex, numerous, and dependent on the nature of the solvent (Table I). In benzene, nitrogen is evolved and some of the products (benzoic acid and 2,5-diphenyl-1,3,4-oxadiazole) suggest the loss of an oxygen atom from dibenzoyl diimide to the benzoyl radical. Other products which may involve participation of the solvent, are benzaldehyde, biphenyl and benzoyl hydrazines. Benzoyl chloride and trichloroacetophenone are formed in carbon tetrachloride. In ethanol, ethyl benzoate and benzoic acid are formed as well as nitrogen, benzaldehyde and benzoylhydrazines.

The products and the initiation of polymerization indicate that radicals are generated in all of the solvents investigated. The kinetics are complex, a result understandable in view of the concurrent disappearance of the dibenzoyl diimide by decomposition, induced and otherwise, and by the addition of hydrogen or radicals to the azo linkage. We have not found an inhibitor capable of suppressing the complicating reactions and simplifying the kinetics. Nevertheless, the accelerating effect of electron-withdrawing substituents, of acids and of nucleophilic solvents is so large as to be unmistakable.

The solvents fall into two categories separated by orders of magnitude in the decomposition rate. The slow category includes carbon tetrachloride, benzene and benzonitrile. Benzene and benzonitrile give very much the same rate although the latter has a considerably higher dielectric constant. The fast category consists of the nucleophilic solvents such as amines and alcohols and mixtures of these with benzene, benzonitrile or carbon tetrachloride. Carbon tetrachloride–ethanol gives a very fast and autocatalytic decomposition because benzoyl chloride formed by radical attack on the carbon tetrachloride reacts with the ethanol to form hydrogen chloride, a very powerful catalyst for the decomposition. Benzene–ethanol mixtures,

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[1] This research was supported by the Office of Naval Research, United States Navy. Reproduction in whole or in part is permitted for any purpose of the United States Government.

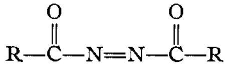
[2] This paper is based on the doctoral dissertation of W. Bradford Bond, Florida State University, 1955.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **75**, 4115 (1953).

[5] L. Michaelis, *Chem. Revs.*, **16**, 243 (1935).

TABLE I

DECOMPOSITION OF 

$R-\overset{O}{\overset{\|}{C}}-N{=}N-\overset{O}{\overset{\|}{C}}-R$

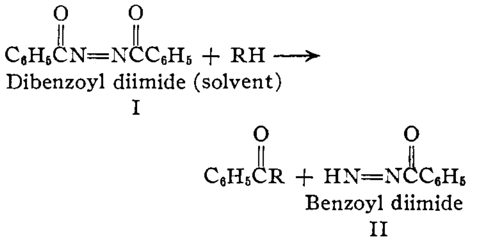
			Products, moles per mole of diimide							
R,R'	Solvent	Temp., °C.	(RCO-NH)$_2$	(RCO)$_2$-NNHR	N_2[a]	RCOOH	RCOOEt	RCHO	2,5-Diaryl-1,3,4-oxadiazole	Other
C_6H_5[b]	C_6H_6[c]	110	0.12			0.06		0.08[e]	0.25	0.23 Biphenyl, 3.7 wt. % of alkali-soluble material, probably mixed di- and tribenzoylhydrazines
C_6H_5[b]	C_6H_6[d]	100	.10			.28		.12[e]	.14	
p-$O_2NC_6H_4$,[k] p-$MeOC_6H_4$	C_6H_6[c]	110	.07[f]			.08,[i] 0.13[j]		0.01,[g] 0.02[h]	.23[f]	0.11 p-Nitrobiphenyl, 0.04 p-methoxybiphenyl, 12 wt. % alkali-soluble material other than RCOOH
C_6H_5	CCl_4	100			0.58				.19	Benzoyl chloride and/or trichloroacetophenone, 0.98,[l] 0.94,[m] 1.12[n]; benzoyl chloride, 0.72[o]; 3.6 wt. % of an acid m.p. 130–133° after basic hydrolysis
C_6H_5[p]	C_6H_5CN–[q] $C_6H_5NH_2$	26	.08	0.03	.76	Trace				1.14 benzanilide; small amount of presumed hydrobenzoin dibenzoates, m.p. 212–215°; total nitrogen recovery, 87%; total benzoyl group recovery 70%
C_6H_5[r]	EtOH[s,t]	Room	.10	0.07	.83	0.52	0.12[l]	0.61[u,v]		0.70 total acids by titration with alkali to phenolphthalein end-point
C_6H_5[r]	EtOH[s,w]	Room	.10		.83	.85	.13[l]	.38[x,v]		
C_6H_5[r]	EtOH[s,y]	Room	.19			.17		None[bb]		
p-$O_2NC_6H_4$, p-$MeOC_6H_4$	EtOH[s,t]	Room	.12[f]			.09,[i] 0.20[j]	.15,[i] 0.25[j]	None[bb]		0.10 p,p'-dicarbethoxyazoxybenzene[z]
p-$MeOC_6H_4$	EtOH[w]	25	.25			.51	.35	.08[aa]		
C_6H_5	EtOH–CCl_4 50%[w]	Room	.05	.04		.23		None[bb]		0.80 HCl and benzoyl chloride;[cc] 0.96 less reactive organic chloride[dd]
p-$O_2NC_6H_4$, p-$MeOC_6H_4$	EtOH–CCl_4 50%[w]	Room	.28							0.63 HCl and aroyl chloride[cc]
C_6H_5	Pyridine	Room	.05	.43					.07	
C_6H_5	C_6H_5CHO[w]	Room		.45						Small amount of presumed hydrobenzoin dibenzoates, m.p. 214–215°

[a] From volume of evolved gas. [b] Concentration about 1%. [c] Degassed. [d] Not degassed. [e] The neutral fractions gave a mixture of 2,4-dinitrophenylhydrazones and gave this yield of benzoic acid on oxidation with Tollens reagent. [f] $R_1 = p$-$O_2NC_6H_4$, $R_2 = p$-$CH_3OC_6H_4$. [g] R = p-$NO_2C_6H_4$, as 2,4-dinitrophenylhydrazone. [h] R = p-$CH_3OC_6H_4$, as 2,4-dinitrophenylhydrazone. [i] R = p-$NO_2C_6H_4$. [j] R = p-$CH_3OC_6H_4$. [k] 50% of the p-$NO_2C_6H_4$ and 49% of the p-$CH_3OC_6H_4$ accounted for. [l] As C_6H_5COOH isolated on hydrolysis of the reaction mixture. [m] As $C_6H_6CONH_2$ isolated on ammonolysis of the reaction mixture. [n] As $C_6H_5CONHC_6H_5$ isolated on anilinolysis of the reaction mixture. Air was present in this run but not in the other CCl_4 runs. [o] As aniline hydrochloride isolated from the anilinolysis of the reaction mixture. The other figures (*l–n*) are higher, probably because solvolysis of trichloroacetophenone does not give chloride ion. [p] Concentration of diimide about 2%. [q] Degassed or nitrogen saturated. [r] Concentration 1 to 2%. [s] Water concentration less than 0.0055 *M*, or less than 6 mole % of the diimide. [t] Oxygen was eliminated by refluxing for three hours in a stream of pre-purified nitrogen bubbled through the solvent. While the diimide was added the nitrogen stream was increased momentarily and then the magnesium perchlorate outlet tube was replaced. Except in the nitrogen evolution experiment the nitrogen bubbling was continued overnight. [u] As semicarbazone and as 2,4-dinitrophenylhydrazone. [v] No acetaldehyde. [w] Under air. [x] As 2,4-dinitrophenylhydrazone and by oxidation to benzoic acid with weakly alkaline permanganate. A control mixture of benzaldehyde and ethyl benzoate analyzed by oxidation of the benzaldehyde in this way followed by saponification of the ethyl benzoate gave accurate values for both components as benzoic acid. [y] Shaking with mercury. The reaction is faster under these conditions but little or no mercury is taken up. [z] For an analogous reaction, see G. S. Hammond and A. Ravve, THIS JOURNAL, **73**, 1891 (1951). [aa] Determined as anisic acid. [bb] Aldehydes absent entirely. [cc] Chloride immediately available as AgCl on treating with alcoholic silver nitrate at room temperature. [dd] Additional silver chloride formed by warming the volatile products with alcoholic silver nitrate on the steam-bath.

on the other hand, give a slower decomposition than ethanol alone.

The rates in solvents of the nucleophilic category fall in the order that might be expected on the basis of experience with nucleophilic solvolysis reactions. Thus wet ethanol is faster than absolute ethanol, while aniline is faster than methanol, methanol faster than ethanol, and ethanol faster then benzyl alcohol which in turn is still very much faster than benzene.

It is possible that nucleophilic solvents containing active hydrogen produce radicals indirectly by an initial solvolysis of dibenzoyl diimide to the unknown but possibly very unstable benzoyl diimide.



$$C_6H_5\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}C_6H_5 + RH \longrightarrow$$

Dibenzoyl diimide (solvent)
I

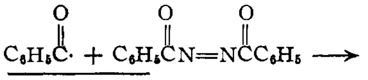
$$C_6H_5\overset{\overset{O}{\|}}{C}R + HN{=}N\overset{\overset{O}{\|}}{C}C_6H_5 \quad \text{(Eq. 1)}$$

Benzoyl diimide
II

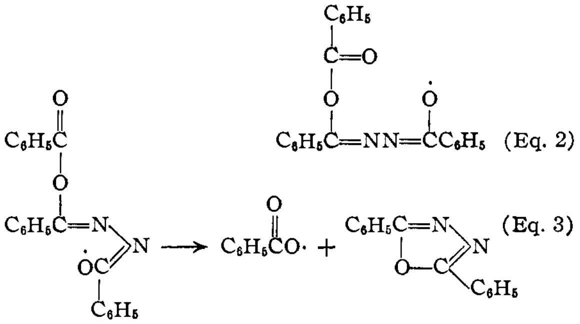
This hypothesis will not explain the rapid reaction in dimethylaniline[6] or in pyridine, however. Other objections to it are the rather low yield of ethyl benzoate from the decomposition of dibenzoyl diimide in ethanol and the fact that the yield of ethyl anisate from the decomposition of dianisoyl diimide in ethanol is higher than the yield of ethyl benzoate from the decomposition of dibenzoyl diimide. That is, the effect of substituents on the rate in ethanol does not parallel the effect on the yield of ester. The authors therefore prefer the explanation that in this initial step the reaction produces solvated benzoyl radicals rather than such products as ethyl benzoate. Ethyl benzoate and anisate can be formed from the radical–ethanol complexes by loss of hydrogen to another radical or to a molecule of the dibenzoyl diimide.

Benzoic acid is a minor product in benzene and a major one in absolute ethanol, even in thoroughly nitrogen-washed or degassed solvent. In the case of ethanol the acid has been shown to be present in the reaction mixture by titration as well as by isolation. It is therefore not formed from the benzaldehyde during the working up of the mixture. The second oxygen needed for the conversion of benzoyl radical to benzoic acid must be abstracted from the dibenzoyl diimide in the case of the benzene reaction. In ethanol it probably comes from the solvent.

The yield of benzoic acid from the decomposition in benzene is very much increased when air is present and this increase is balanced by a corresponding decrease in the amount of 2,5-diphenyl-1,3,4-oxadiazole formed. It is therefore likely that benzoyl radicals plus dibenzoyl diimide give benzoyloxy radicals plus diphenyloxadiazole, as in equations 2 and 3, but that the benzoyl radicals are diverted by oxygen if that is present.



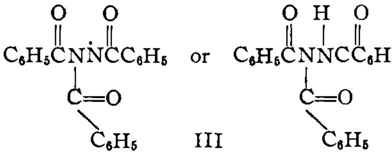
$$C_6H_5\overset{\overset{O}{\|}}{C}\cdot + C_6H_5\overset{\overset{O}{\|}}{C}N{=}N\overset{\overset{O}{\|}}{C}C_6H_5 \longrightarrow$$



(Eq. 2)

(Eq. 3)

An analogy for reaction 2 is the production of hydrobenzoin dibenzoate from benzoyl radicals and benzaldehyde[7] while the internal radical displacement of oxygen by oxygen is analogous to the formation of phenyl salicylate from 2-phenoxybenzoyloxy radical.[8] Since the benzoyloxy radicals generated in the decomposition of benzoyl peroxide are known to be increasingly decarboxylated at higher temperatures the yield of benzoic acid in this experiment at 110° will not equal the yield of diphenyloxadiazole. Another possible source of diphenyl oxadiazole is tribenzoylhydrazine, which gives diphenyloxadiazole and benzoic acid. This reaction can be eliminated because we have found that it produces more than the observed amount of benzoic acid at 110, probably directly as benzoic acid rather than as benzoyloxy radicals. Finally, radicals or tribenzoylhydrazines of the type III can be eliminated as intermediates because only one diphenyloxadiazole is formed in the decomposition of p-methoxy-p'-nitrodibenzoyl diimide.



III

In absolute ethanol there is no isolable amount of diphenyloxadiazole formed and the considerable amount of benzoic acid must derive its second oxygen atom from the solvent. At least two possibilities are apparent, the more likely one being the removal of the ethyl group in some way from a solvated benzoyl radical or from a solvated dibenzoyl diimide molecule. Neither ethylene nor compounds of the type REt have been identified. A chain reaction involving free hydroxyl radicals seems unlikely. The experimental conditions would appear to preclude atmospheric oxygen or water as sources of oxygen.

Polar Effects in Benzoyl Peroxide Decomposition

The rate of the radical decomposition of benzoyl peroxide is affected by polar substituents and is subject to the $\rho\sigma$-treatment.[3] Benzoyl peroxide differs from dibenzoyl diimide in several ways, however. A p-methoxy and p'-nitro substituent in a polar medium cause a change to a polar mechanism which is not the case with dibenzoyl diimide.[9] Benzoyl peroxide radical decomposition is

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(6) L. Horner and W. Naumann, *Ann.*, **587**, 81 (1954).

(7) F. F. Rust, F. H. Seubold and W. E. Vaughan, This Journal, **70**, 3258 (1948).

(8) D. F. DeTar and A. Hlynsky, *ibid.*, **77**, 4411 (1955).

(9) J. E. Leffler, *ibid.*, **72**, 67 (1950).

not very sensitive to acid catalysis.[10] The decomposition of benzoyl peroxide in pyridine is only somewhat faster than it is in benzene, suggesting chains rather than a direct reaction between the peroxide and the pyridine. The very rapid reaction with other amines and the reaction with phenols may well be in part direct as has been suggested.[11] In either case certain reaction products at the *o*-position find a ready explanation if it is assumed that a nucleophilic solvent can interact with the carbonyl group of the peroxide or of the benzoyloxy radical to form a cyclic intermediate. One example is the formation of *o*-hydroxy-N-benzoyldiphenylamine from diphenylamine.[12] Other examples are the formation of 2,2'-bisdimethylaminobiphenyl from dimethylaniline[13a] and the formation of the same *o*-hydroxyxylyl benzoate from isomeric *m*-xylenols.[13b]

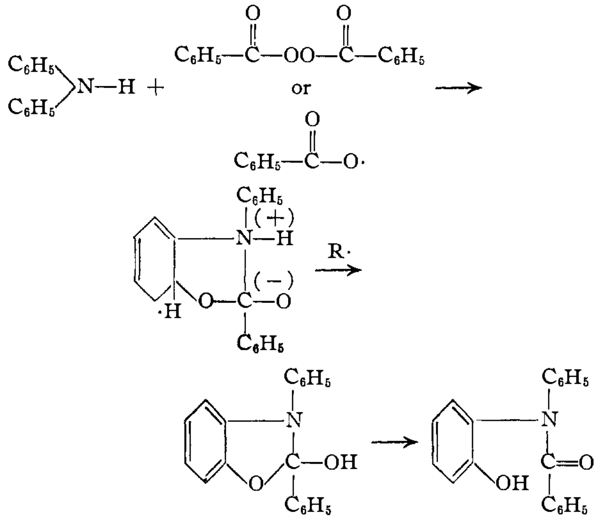

TABLE II

DECOMPOSITION KINETICS OF DIBENZOYL DIIMIDES

Initial diimide concn., mole/liter	Temp., °C.	10^6k, sec.$^{-1}$	Notes
Dibenzoyl diimide in benzene			
0.03	100	7.33 ± 0.40	
.01		7.79	a
.01		7.60	
.01	92	3.14	
.01		2.91	a
.01	92	10.9	
.01		8.7	b
.01	92	27.2	
.01		30.5	c
.02	75	0.54 ± 0.08	
.01		.70	d
.007		.56	
.01	75	.55	
.007		.44 ± 0.18	d,e
p-Methoxy-*p*'-nitrodibenzoyl diimide in benzene			
0.025	100	40.1 ± 2.5	a
.012		35.2 ± 3.2	
.007		23.4	
.007	75	5.4 ± 0.5	a,f
.005		3.8 ± .5	
.005		5.1 ± .5	
.0025		4.2 ± .6	
.0025		8.6 ± 1.1	
Dibenzoyl diimide in benzonitrile			
0.02	100	6.9	a
.02		7.3	
.02		7.3	
.005		8.6 ± 0.6	
Dibenzoyl diimide in ethanol			
0.008	19.69	75.6	e
.005		72.8	
.012		81.0	
.005		71.0	
.019		91.1	
.021		85.5	
.019		87.7	
.023		86.9	
.005		80.1	
.018		95.9	
.013		83.8	
.0066	19.69	77.1	e,g
.0083		79.9	
.0125		80.8	
.0135	19.69	124	e,h
.0055	34.13	173	
.010	34.14	182	e
.0048	34.06	188	
.0089	34.21	185	
.0095	34.20	218	e,i
.0085	34.21	220	
.024		233	
.0043		223	
.012	34.21	246	e,j
.0053	25.00	108	e
.0137		111	
Dibenzoyl diimide in benzyl alcohol			
0.0051	61.90	137	k
Dibenzoyl diimide in methanol			
0.0081	27.0	969	e
p-Methoxy-*p*'-nitrodibenzoyl diimide in 50% ethanol-benzene			
0.010	19.69	957	e
.015		939	
.022		1170	
.016		1010	
.009	25.95	1630	l
p,*p*'-Dianisoyl diimide in ethanol			
0.0046	25.0	9.1	e
.0112	25.0	10.9	

[a] Degassed. [b] Degassed, 0.0114 *M* benzoic acid added. [c] Degassed, 0.094 *M* benzoic acid added. [d] Estimated from initial rate. [e] Air present. [f] Estimated from first 20–30% of the decomposition. [g] With 0.0057, 0.0099 and 0.0226 *M* benzaldehyde added. [h] With 0.0287 *M* benzoic acid added. [i] With 0.093 *M* water. [j] With 0.140 *M* water. [k] Under nitrogen. Followed by gas evolution. [l] With 2.5% acrylonitrile.

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(10) P. D. Bartlett and J. E. Leffler, THIS JOURNAL, **72**, 3030 (1950).

(11) L. Horner and K. Scherf, *Ann.*, **573**, 35 (1951); J. E. Leffler, THIS JOURNAL, **72**, 3809 (1950).

(12) S. Gambarjan, *Ber.*, **42**, 4003 (1909).

(13) (a) L. Horner and C. Betzel, *Ann.*, **579**, 175 (1953); (b) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 3189 (1949).

Kinetics

The rate of decomposition of the dibenzoyl diimides was measured by a standard spectrophotometric technique utilizing the azo group absorption band at 470 mμ. One run in benzyl alcohol was followed by the nitrogen evolution method.

The rate constants are given in Table II. In benzene, using degassed and sealed ampoules, the disappearance of dibenzoyl diimide at 100° follows a first-order rate law to 80% of completion and the rate constants are insensitive to a threefold increase in initial concentration. Benzoic acid catalyzes the decomposition but is not produced in sufficient amount at 100° to affect the kinetic order noticeably. The decomposition of *p*-methoxy-*p*′-nitrodibenzoyl diimide in benzene at 100° is faster than that of dibenzoyl diimide but the rate constants decrease with decreasing initial diimide concentration.

In contrast to the kinetic simplicity prevailing at 100°, first-order rate plots for the decompositions in benzene at 75° are markedly curved, the actual order within a single run being less than unity (Fig. 1). The curvature may be due in part to product catalysis, especially catalysis by benzoic acid. The tabulated first-order rate constants at 75° are estimated from the initial rates and are not precise. Attempts to eliminate the curvature by using possible chain inhibitors such as acetanilide, acrylonitrile, hydroquinone, diethyl malonate and air were unsuccessful. The rate is enhanced by acetanilide (Fig. 1). In view of these complexities no activation parameters have been calculated from our data.

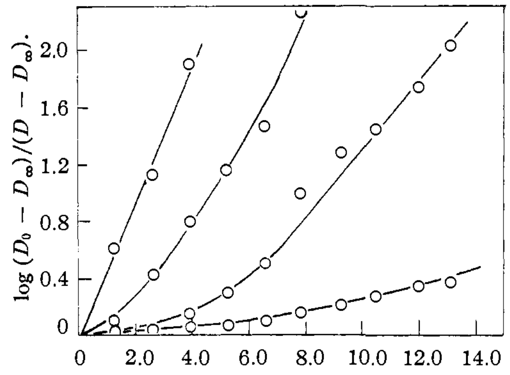

Fig. 1.—Dibenzoyl diimide in benzene at 75°. Reading from left to right: initial concentration 0.0102 *M* but with decomposition products added; initial concentration 0.0307 *M* with 0.1 *M* acetanilide added; initial concentration 0.0307 *M*; initial concentration 0.0102 *M*.

The decomposition of dibenzoyl diimide in benzonitrile at 100° is first order and very much like that in benzene. In carbon tetrachloride the decomposition is roughly ten times as fast as in benzene but the first-order rate constant decreases as the reaction proceeds (Fig. 2).

The decomposition of dibenzoyl diimide in ethanol at 25° is nicely first order within a run, but this simplicity is specious since the reaction in the latter part of the run is accelerated by the benzoic acid produced. Dianisoyl diimide in ethanol decomposes more slowly than dibenzoyl diimide, while the decomposition of *p*-methoxy-*p*′-nitrodibenzoyl diimide was too fast for convenient measurement and was therefore studied in 50% ethanol–benzene.

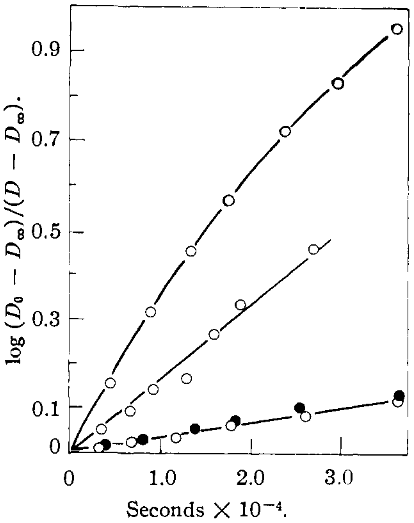

Fig. 2.—Dibenzoyl diimides in inert solvents at 100°: top curve, dibenzoyl diimide in carbon tetrachloride; middle curve, *p*-methoxy-*p*′-nitrodibenzoyl diimide in benzene; bottom curve, dibenzoyl diimide in benzonitrile (open circles) and in benzene (filled circles).

Whereas dilution of ethanol with benzene slows down the decomposition, carbon tetrachloride has the opposite effect and the reaction is drastically autocatalytic due to the formation of hydrogen chloride (Fig. 3). The reaction of ethanol with benzoyl chloride is fast enough to provide hydrogen chloride during the run and the decomposition of dibenzoyl diimide in ethanolic hydrogen chloride takes only a few seconds at room temperature.[14]

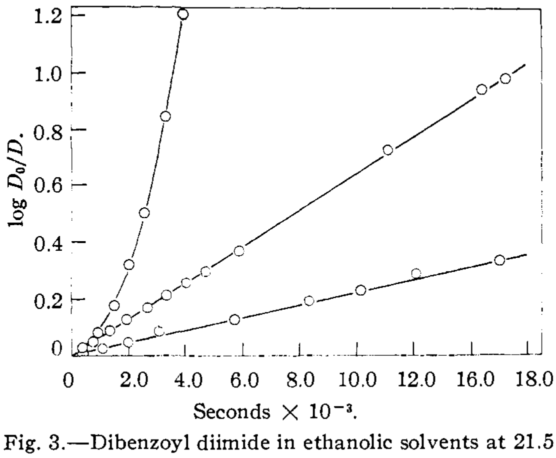

Fig. 3.—Dibenzoyl diimide in ethanolic solvents at 21.5°: top curve, 50% ethanol–carbon tetrachloride; middle curve, ethanol; bottom curve, 50% ethanol–benzene.

Experimental

Dibenzoyl Diimide.—(a) Dibenzoylhydrazine, m.p. 240–242°,[15] was converted to the sodium salt in ethanol and then

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[14] E. Mohr, *J. prakt. Chem.*, **70**, 281 (1904).

[15] H. H. Hatt, "Organic Syntheses," Coll. Vol. II, Ed. by A. H. Blatt, John Wiley and Sons, New York, N. Y., 1943, p. 208.

to the mercury salt.[16] Bromine oxidation was carried out with a 1:1 mole ratio instead of the 2:3 bromine to mercury salt ratio recommended by Stollé.[16] High boiling petroleum ether was used as the solvent and the product isolated after filtration by cooling the red solution in a Dry Ice–acetone-bath; m.p. 119.5–121.5° (ligroin).

(b) The procedure of Horner and Naumann[17] gives lower yields but is more convenient. The base-soluble hydrazide was oxidized with sodium hypochlorite, the water-insoluble diimide being extracted into a supernatant benzene layer as fast as it was formed. Benzene is preferable to ether as the second layer.

_p_-Methoxy-_p′_-nitrodibenzoylhydrazine.—Anisic hydrazide,[18] 3.3 g. 0.02 mole, and _p_-nitrobenzoyl chloride, 3.7 g., 0.02 mole, were dissolved in 25 ml. of dry pyridine, and the mixture warmed to dissolve the chloride. Clusters of yellow crystals formed on standing. Water was added and the _p_-methoxy-_p′_-nitrodibenzoylhydrazine removed by filtration. The yield was 1.61 g., m.p. 257.6–260.0°, after recrystallization from ethanol, m.p. 258–261°.

Anal.[19]—Calcd. for $C_{15}H_{13}N_3O_5$: C, 57.2; H, 4.16; N, 13.3. Found: C, 57.4, 57.5; H, 3.99, 4.15; N, 13.5, 13.4.

_p_-Methoxy-_p′_-nitrodibenzoyl Diimide.—(a) The hydrazide, 16.1 g., 0.051 mole, was dissolved in a large volume of refluxing ethanol. The solution was cooled slightly and 2.4 g., 0.10 mole, of sodium metal dissolved in ethanol added slowly with stirring, followed rapidly by 14.0 g., 0.052 mole, of mercuric chloride dissolved in ethanol. The solution becomes dark red on addition of the sodium ethoxide, and the addition of the mercuric chloride produces the mercury salt as a dense yellow precipitate which was removed while the ethanol was still warm. The yield of mercury salt was 17.1 g., 0.033 mole. To a stirred slurry of the carefully dried mercury salt in 300 ml. of dry ligroin was added dropwise 5.3 g. of bromine, 0.033 mole, in ligroin. The mixture was filtered immediately and the precipitate extracted with 50% high-boiling ligroin–benzene. On recrystallization, 2.59 g. of orange crystals, m.p. 122–125°, was obtained. Further recrystallization from 75% ligroin–benzene gave a product melting at 130–132°.

Anal.[19] Calcd. for $C_{15}H_{11}N_3O_5$: C, 57.50; H, 3.54. Found: C, 57.50, 57.59; H, 3.51, 3.25.

(b) The general method of Horner and Naumann[17] was also used. The sodium salt of this diacylhydrazine is not so soluble in water as that of dibenzoylhydrazine. An emulsion forms. The oxidation is faster and the product much less stable, so that the benzene phase must be worked up rapidly.

Di-_p_-anisoyl Diimide.—Di-_p_-anisoylhydrazine, m.p. 225–230°, was converted, as described for the benzoyl compound, into the mercury salt in 78% yield. The mercury salt was treated with bromine in high boiling petroleum ether as in the other procedure, the product frozen out in Dry Ice–acetone and recrystallized from ligroin as yellow-orange needles, yield 24–30%, m.p. 131.5–132.0°.[20] Horner and Naumann report[17] the m.p. as 132°.

2-_p_-Methoxyphenyl-5-_p_-nitrophenyl-1,3,4-oxadiazole.—Although 2,5-diphenyl-1,3,4-oxadiazole is readily prepared from the corresponding diacylhydrazine *via* the dichlorobenzalazine, a similar route failed to give 2-_p_-methoxyphenyl-5-_p_-nitrophenyl-1,3,4-oxadiazole. Treatment of the diacylhydrazine with phosphorus pentachloride in carbon tetrachloride gave a yellow solid, m.p. 135–136° after recrystallization from carbon tetrachloride, containing a little acetyl chloride. This presumed dichloride gave only the starting diacylhydrazine on refluxing with acetic acid–hydrochloric acid. It was not further investigated. Instead, one gram of the diacylhydrazine was refluxed in benzene with the addition of 2–5 g. of phosphoric pentoxide over a period of three days. The reaction mixture after filtration and washing to remove inorganic acids was dried and freed of solvent. The sodium hydroxide-insoluble part of the residue was chromatographed on alumina and the 2-_p_-methoxyphenyl-5-_p_-nitrophenyl-1,3,4-oxadiazole eluted with 5% ether in benzene. It melted at 228–229°, weight 0.32 g., bright yellow. It was shown by mixed melting point and infrared spectrum to be identical with the heterocycle isolated from the decomposition of _p_-methoxybenzoyl-_p′_-nitrobenzoyl diimide in benzene. The latter material was analyzed.[19] *Anal.* Calcd. for $C_{15}H_{11}N_3O_4$: C, 60.60; H, 3.73; N, 14.14. Found: C, 60.62, 60.82; H, 3.55, 3.43; N, 14.20, 13.92.

Diethyl _p,p′_-Azoxybenzoate.—_p,p′_-Azoxybenzoic acid,[21] or more probably a mixture of that compound and _p,p′_-azobenzoic acid, was converted to the acid chloride and ester.[22] The ester, red crystals m.p. 114–116°, was heated with hydrogen peroxide in acetic acid to convert the azo impurity to the azoxy compound. The product recrystallized from ethanol consisted of yellow needles, sintering at 114–115° and melting at 121–122°. Ethyl _p,p′_-azoxybenzoate exists in an anisotropic form which appears at the sintering point, 114–115°, and disappears at the melting point, 122.5°.[23] It proved to be identical by mixed melting point and infrared spectrum with a compound isolated from the decomposition of _p_-methoxy-_p′_-nitrodibenzoyl diimide in ethanol.

Solvents.—Thiophene-free benzene was washed several times with concentrated sulfuric acid, 5% sodium bicarbonate and water. It was then dried over calcium chloride and distilled from sodium through a fractionating column, keeping a middle fraction.

Carbon tetrachloride was stirred 0.5 hour with concentrated sulfuric acid, washed with water, sodium bicarbonate and water, then dried over potassium carbonate and distilled from phosphorus pentoxide through a fractionating column, keeping a middle fraction.

Commercial benzonitrile even after vacuum distillation and discarding a fore-run was found to contain aniline. Dibenzoyl diimide at a concentration of 0.03 *M* decomposes in the solvent thus prepared with first-order kinetics and a half-life of 9 minutes at 26°, whereas the half-life in a more elaborately purified material is 1500 minutes at 100°. For further purification the benzonitrile was washed twice with dilute sulfuric acid, with dilute sodium hydroxide and with water until neutral, then dried over calcium chloride and distilled through an all-glass helices-packed column, keeping the fraction boiling at 70° and 12 mm.

Absolute ethanol was prepared by the Lund and Bjerrum method.[24] Karl Fischer titration[25] showed a maximum water concentration of 0.0055 *M*.

Ethanol containing 0.093 *M* water was reagent grade absolute ethanol, the water content determined by Karl Fischer titration.

Absolute methanol was supplied by Dr. Anthony Baccarella.[26]

Benzyl alcohol was purified by the method of Martin and George.[27]

Merck benzaldehyde was distilled in a nitrogen atmosphere at 2 mm., a forerun being discarded.

Commercial pyridine was distilled from barium oxide after several hours of refluxing. A middle fraction distilling at 114–115° was then redistilled from phosphorus pentoxide, collecting the fraction boiling at 115°.

Decomposition Products.—The decomposition products were isolated by conventional methods and identified by mixed melting points with authentic samples unless otherwise indicated. Oily by-products appeared at all stages of the separation procedures indicating a mixture much more complicated than would be suggested by the number of isolated and identified compounds.

Polymerization.—Acrylonitrile is polymerized by the decomposition of dibenzoyl diimide in acrylonitrile at 75°, in benzene at 75°, in carbon tetrachloride at 75°, in ethanol at 50°, in ethanol–carbon tetrachloride at 50°, in ethanol–ben-

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(16) R. Stollé, *Ber.*, **45**, 273 (1912).

(17) L. Horner and W. Naumann, *Ann.*, **587**, 93 (1954).

(18) T. Curtius and H. Melsbach, *J. prakt. Chem.*, **81**, 548 (1910).

(19) Analyses by Clarke Microanalytical Laboratory.

(20) A minor second fraction melting at 112–114° was consistently found. Its analysis is close to that of dianisoyl diimide. *Anal.*[19] Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.43; H, 4.73. Found: C, 64.23, 64.00; H, 4.69, 4.52.

(21) H. W. Galbraith, E. F. Degering and E. F. Hitch, THIS JOURNAL, **73**, 1323 (1951).

(22) D. Vorländer, *Trans. Faraday Soc.*, **29**, 902 (1933).

(23) F. Meyer and K. Dahlem, *Ann.*, **326**, 334 (1903).

(24) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 359.

(25) D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., THIS JOURNAL, **61**, 2407 (1939).

(26) A. L. Baccarella, Doctoral Dissertation, Florida State University, 1953.

(27) A. R. Martin and C. M. George, *J. Chem. Soc.*, 1413 (1933).

zene at 50°, and in tetralin at 92°.[28] All polymerization experiments were carried out in sealed and degassed ampoules, the polymer isolated by precipitation with methanol and compared with a control experiment. Polymerization of acrylonitrile is also induced by dianisoyl diimide in ethanol–carbon tetrachloride at 50° and in benzene at 75° and by *p*-methoxy-*p'*-nitrodibenzoyl diimide in ethanol–carbon tetrachloride at 50°, in ethanol–benzene at 50°, and in benzene at 75°. Dibenzoyl diimide failed to initiate polymerization of acrylonitrile in benzonitrile containing aniline at 75°. However, amines have been reported to inhibit the polymerization of acrylonitrile.[29] In none of our qualitative polymerization experiments has there been any noticeable effect of the acrylonitrile on the rate. This was also the case in a kinetic experiment in which *p*-methoxy-*p'*-nitrodibenzoyl diimide was decomposed in 50% ethanol–benzene containing 1% of acrylonitrile. Acrylonitrile does not inhibit the decomposition.

TALLAHASSEE, FLORIDA

[28] L. Horner and W. Naumann, *Ann.*, **587**, 93 (1954), reported no polymerization in refluxing acrylonitrile or in refluxing acrylonitrile–tetralin under carbon dioxide.

[29] C. J. Stehman, U. S. Patent 2,607,795, August 19, 1952.

[CONTRIBUTION FROM THE SANITARY CHEMISTRY BRANCH, CHEMICAL CORPS MEDICAL LABORATORIES]

Kinetics of the Reaction of Isopropyl Methylphosphonofluoridate with Catechols at 25°

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The reaction of Sarin (isopropyl methylphosphonofluoridate) with catechol or one of its nuclearly substituted derivatives is of second order; the rate is proportional to the first power of both the Sarin concentration and singly dissociated catecholate ion. The second-order rate constant (l. mole^{-1} min.$^{-1}$) for the reaction of a particular catechol derivative may be expressed as a function of the basic dissociation constant of the catecholate ion, according to the equation $k_2 = 2.57 \times 10^{-6} K_B^{0.89}$. The enhanced reactivity of the catechols toward Sarin as compared to phenols, and the relationship of k_2 to K_B are in agreement with the proposed reaction mechanism.

Sarin (isopropyl methylphosphonofluoridate) is among the more potent of the German nerve gases.[1] It resembles diisopropylphosphorofluoridate in chemical behavior but reacts more rapidly with most reagents. Our purpose, in the present study was to obtain an understanding of the behavior of catechols,[2] which react more rapidly than phenols,[3,4] with nerve gases, using Sarin as a model compound, in order to permit prediction of reactive catechol structures. It has been shown[3] that the reaction rates of phosphorofluoridate esters with catechols, which, in aqueous solution, increase with rising *p*H, are consistent with the assumption that the rate is dependent upon the concentrations of the dissociated catecholate ions; but the effect of substituents on the aromatic ring has not, up to now, been clarified.

At constant *p*H the rate of disappearance of Sarin when a catechol is present in sufficient excess concentration is of first order. The first-order rate constant thus obtained, corrected for spontaneous hydrolysis, (*i.e.*, $k_1 - k_s$) where k_1 is the observed first-order rate constant, k_s is the rate constant for hydrolysis of Sarin in catechol-free aqueous solution at the *p*H and buffer strength of the experiment, is proportional to the catechol concentration. Thus, an apparent second-order rate constant $k_2' = (k_1 - k_s)/[C]$ may be calculated, where [C] is the molar concentration of catechol plus catecholate ion, and k_1 and k_s are as previously defined.

The apparent second-order rate constant, k_2', for the reaction of unsubstituted catechol with Sarin over the *p*H range 6–9 varies directly with hydroxyl ion concentrations, but the corresponding constants for the more acidic mononitrocatechols approach constancy in the regions of the greatest monodissociation (Fig. 1). While k_2' varies with *p*H, $k_2 = '(k_1 - k_s)/[C^-]$ (where $[C^-]$ is the concentration of monocatecholate ion) remains constant over a range of *p*H values (Table I).

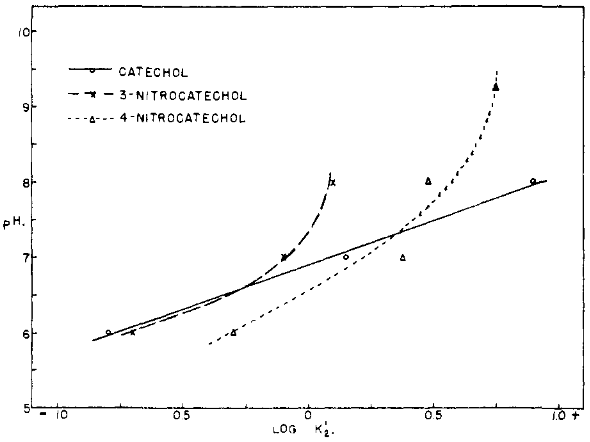

Fig. 1.—Plot of the log k_2' against *p*H for reactions between Sarin and catechol, 3-nitrocatechol and 4-nitrocatechol.

TABLE I

EFFECT OF *p*H ON RATE CONSTANTS FOR REACTION OF 3-NITROCATECHOL WITH SARIN

*p*H	k_2' (l. mole^{-1} min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)	*p*H	k_2' (l. mole^{-1} min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)
6	0.27	1.48	7	0.80	1.16
6	.24	1.33	8	1.31	1.37
7	.81	1.18	8	1.25	1.31

When $[H^+]$ = hydronium ion concentration, and K_A is known, $[C^-] = K_A[C]/([H^+] + K_A)$.

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[1] Anon., *Chem. Eng. News*, **31**, 4676 (1953).

[2] "Catechol" will refer to the class of compounds that includes the parent compound (unsubstituted catechol) and its nuclearly substituted derivatives.

[3] B. J. Jandorf, T. Wagner-Jauregg, J. J. O'Neill and M. Stolberg, THIS JOURNAL, **74**, 1521 (1952).

[4] K. B. Augustinsson, *Acta Chem. Scand.*, **6**, 949 (1952).