lapped by the tail of the $\pi \rightarrow \pi^*$ transition. The corrected *blue-shift* corresponds to an energy of 2.6 kcal. which is of the same order as the value 2.2 kcal. obtained from the infrared data.

The infrared work with azobenzene indicates a very small association constant of azobenzene with ethanol. Thus although the hydrogen-bonded azobenzene molecule might have its $n \rightarrow \pi^*$ transition moved by a considerable amount to higher energies compared with the non-hydrogen bonded molecule, the apparent maximum of azobenzene in ethanol would correspond to the average spectrum of mainly uncomplexed azobenzene with a few per cent. of hydrogen bonded molecules. This would account for the very small (160 cm.$^{-1}$) *blue-shift* of the azobenzene $n \rightarrow \pi^*$ transition from methylcyclohexane to ethanol which is actually observed.

Polar solvents like ethers and nitriles which are not expected to hydrogen bond strongly with the solute molecule also cause a *blue-shift* of $n \rightarrow \pi^*$ absorption bands. This shift is generally much less than the *blue-shift* caused by hydrogen bonding in hydroxylic solvents, but is nevertheless appreciable. Preliminary investigations with propionitrile–hexane mixtures and pyridazine show a similar behavior to ethanol–hexane mixtures, except that the shift is smaller and the concentration of the nitrile necessary to cause the same relative change is much greater. It is unlikely that a definite complex is formed between the nitrile and the pyridazine. But it is probable that the nitrile solvent molecules preferentially orient themselves around the pyridazine molecules, and thus have a higher concentration than average in the neighborhood of the solute molecules.

In conclusion it should be said that the primary object of this work was not to obtain association constants for hydrogen bonding but merely to show that hydrogen bonding is the main influence in the $n \rightarrow \pi^*$ *blue-shift* phenomenon in hydroxylic solvents. The method however has shown itself to be capable of giving accurate association constants from ultraviolet data.

TALLAHASSEE, FLA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY]

Methyl Affinities of Quinones

BY A. REMBAUM AND M. SZWARC

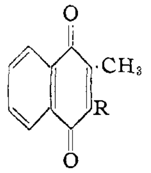
RECEIVED APRIL 12, 1955

Addition of CH_3 radicals to a series of quinones has been investigated. The relative rates of reaction $Q + CH_3 \rightarrow Q\cdot CH$ referred to as methyl affinities, decrease rapidly along the series Q = *p*-benzoquinone (15,200), 1,4-naphthoquinone (4900) phenanthraquinone (700), and *t*-butylanthraquinone (90). This scale of methyl affinities is based on a value of unity for benzene. It was found that a successive methylation of quinones decreases the methyl affinity, the introduction of a methoxy group decreases the reactivity even more. On the other hand, the methyl affinity increases when chlorine atoms are introduced into the molecule. The results are discussed tentatively in terms of reactivities of the C=C double bonds. and in terms of effects due to steric hindrances, the low reactivity of chloranil being the most striking example of the latter effect. By comparing the reactivities of quinones toward methyl radicals and toward styryl radicals, the relative intrinsic reactivity of styryl radical has been determined. It has been found that the latter radical is 2.2 less reactive than the former.

The high reactivity of quinones toward free radicals is well recognized, and this property of quinones accounts for their inhibitory action on many chain processes, such as radical initiated oxidations and the polymerization of vinyl monomers. Although it is generally agreed that reaction (1)

$$Q + R \longrightarrow Q\cdot R \qquad (1)$$

is involved in the inhibitory action of quinones, the nature of the primary adduct Q·R is still unsettled. Some workers suggest that the attacking radical R is added initially to the oxygen atom of a quinone, while others favor the idea that the primary addition process involves the C=C double bond. These conclusions are based on results of investigations into the structure of the *final* products formed in reactions inhibited by quinones. Thus, the isolation of di-ethers like $R\cdot O\cdot C_6H_4\cdot O\cdot R$ is taken as evidence for an O-addition process,[1] while isolation of compounds such as



is considered an argument in favor of an addition mechanism involving the C=C double bond.[2] It seems, however, that the above evidence might be misleading, since an intramolecular rearrangement may accompany the process which converts the *initial* addition product into the *final* product eventually isolated from the reacting mixture. Whether or not such a rearrangement takes place will depend on the nature of the quinone used, on the type of radical attacking, and on the conditions prevailing in the experiment performed.

Quinones differ considerably in their inhibitory power, which can be measured by studying the kinetics of a chain reaction inhibited by these com-

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[1] (a) S. Cohen, THIS JOURNAL, **69**, 1057 (1947); (b) A. F. Bickel and W. A. Waters, *J. Chem. Soc.*, 1746 (1950); (c) F. J. L. Aparicio and W. A. Waters, *ibid.*, 4666 (1952).

[2] (a) D. E. Kvalnes, THIS JOURNAL, **56**, 2478 (1936); (b) L. F. Fieser and A. E. Oxford, *ibid.*, **64**, 2060 (1942).

pounds. For example, in the polymerization of a vinyl monomer inhibited by a quinone, the latter compound and the monomer compete for the growing radical chains

$$R + Q \longrightarrow \text{inactive product} \quad k_1$$
$$R + M \longrightarrow R\cdot \quad k_p$$

Hence, from the kinetic data one may derive a value for k_1/k_p, and such values obtained for a series of quinones provide the required information about the relative rate constants of the inhibitory process. This technique has been used by several investigators,[3-5] whose data are summarized in Table III.

TABLE I

RELATIVE RATE CONSTANTS OF ADDITION OF METHYL RADICALS TO QUINONES, (k_{II}/k_I)

Toluene solution, temp., 65°

Mole %	CH_4/CO_2	k_{II}/k_I	Mole %	CH_4/CO_2	k_{II}/k_I
p-Benzoquinone			2,5-Dimethyl-*p*-benzoquinone		
0.05	0.37	1950	0.05	0.52	820
.05	.35	2160	.10	.39	880
.05	.37	1950	.20	.26	900
.10	.25	1920	2-Methoxy-*p*-benzoquinone		
.20	.14	2100	0.05	0.49	955
Toluquinone			.10	.34	1170
0.05	0.44	1320	2,5-Dichloro-*p*-benzoquinone		
.05	.44	1290	0.03	0.306	4730
.10	.27	1730	.05	.196	5450
.10	.32	1300	.05	.193	5550
.10	.33	1080	2,6-Dichloro *p*-benzoquinone		
.20	.17	1580	0.03	0.290	5000
2-Chlorobenzoquinone			.05	.196	5450
0.05	0.29	3040	.05	.210	4950
.05	.26	3560	Duroquinone		
.10	.16	3630	1.0	0.40	80
.10	.16	3550	1.0	.36	104
			1.0	.34	117
1,4-Naphthoquinone			1.0	.33	118
0.05	0.57	560	Chloranil		
.05	.54	720	0.50	0.60	43
.05	.56	610	0.75	.58	36
.10	.45	615	1.5	.46	34
.20	.29	750	1.5	.40	47
2-Methyl-1,4-naphthoquinone			2,3-Dichloro-1,4-naphthoquinone		
0.05	0.59	460			
.20	.41	390	0.50	0.67	19
.20	.36	500	1.00	.69	5
2,7-Dimethyl-1,4-naphthoquinone			1,2-Naphthoquinone		
			0.05	0.58	500
0.10	0.46	580	.05	.61	390
.20	.35	540	Phenanthraquinone		
.25	.32	515	0.10	0.66	90
2,3-Dimethyl-1,4-naphthoquinone			.20	.61	98
			2-*t*-Butylanthraquinone		
0.20	0.65	60	1.5	0.6	14
0.50	.54	70	2.5	.6	9
1.00	.37	90			

In this paper we report a similar set of data obtained by an entirely different technique. The method used was developed recently by Levy and Szwarc[6] and is based on the following principle. Methyl radicals, generated by the decomposition of acetyl peroxide, react with a solvent according to equation I

TABLE II

Quinone	Methyl affinity	k_{II}/k_{II} *p*-quinone	E^0 (EtOH), volts
p-Benzoquinone	15,200 ± 300	1.00	0.715
2-Methylbenzoquinone	10,400 ± 700	.68	.656
2,5-Dimethylbenzoquinone	6,500 ± 150	.43	.598
Duroquinone	790 ± 120	.052	.466
2-Methoxybenzoquinone	8,000 ± 600	.52	...
2-Chlorobenzoquinone	27,000 ± 900	1.71	.736
2,5-Dichlorobenzoquinone	39,200 ± 3500	2.59	.740
2,6-Dichlorobenzoquinone	38,400 ± 1000	2.54	.748
Chloranil	300 ± 50	0.02	.699
1,4-Naphthoquinone	4,900 ± 230	.32	.484
2-Methyl-1,4-naphthoquinone	3,400 ± 250	.22	.408
2,7-Dimethyl-1,4-naphthoquinone	4,100 ± 250	.27	.407
2,3-Dimethyl-1,4-naphthoquinone	550 ± 60	.036	.340
2,3-Dichloro-1,4-naphthoquinone	90 ± 60	.006	...
1,2-Naphthoquinone	3,400 ± 350	.225	.576
Phenanthraquinone	700 ± 20	.046	.460
2-*t*-Butylanthraquinone	90 ± 15	.006	...
Anthraquinone	....	...	.154

TABLE III

Quinone	Relative reactivity toward Methyl radical	Styryl radical	Allyl acetate radical
p-Benzoquinone	1.00	1.00	1.00
2-Methylbenzoquinone	0.68	0.37	..
2,5-Dimethylbenzoquinone	.43	.076	..
Trimethylquinone	..	.046	..
Duroquinone	.05	.0012	0.08
Trichloroquinone	..	....	1.05
Chloranil	.02	1.67	3.08

$$CH_3 + \text{solvent} \longrightarrow CH_4 + \text{solvent radical} \qquad (I)$$

Addition of a quinone to the solution decreases the amount of methane formed, and it has been shown that such a "loss" of methane is due to reaction (II)

$$Q + CH_3 \longrightarrow Q{\cdot}CH_3 \qquad (II)$$

Hence

$$k_{II}/k_I = \{(\text{amount of } CH_4 \text{ "lost"})/(\text{amount of } CH_4 \text{ formed})\}\ X_S/X_Q$$

where X_S and X_Q denote the mole fractions of solvent and of quinone, respectively.

For purely experimental reasons it is more convenient to base such calculations on the ratios like (CH_4 formed)/CO_2 rather than on the absolute amounts of methane formed. Thus

$$k_{II}/k_I = \{(CH_4 \text{ "lost"}/CO_2)/(CH_4 \text{ formed}/CO_2)\}X_S/X_Q$$

The meaning of the term (CH_4 formed/CO_2) is obvious, while the term (CH_4 "lost"/CO_2) is obtained as a difference between the ratio CH_4/CO_2 resulting from experiments carried out in a pure solvent, *i.e.*, in the absence of a quinone, and the CH_4/CO_2 resulting from an experiment in which quinone is present. Further experimental details, as well as the justification of the method, are given in reference 6.

Experimental

Most of the quinones used in this investigation were kindly supplied to us by Professor L. F. Fieser, whom we thank for

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[3] J. W. Breitenbach and H. L. Breitenbach, *Z. physik. Chem.*, **A190**, 361 (1942).

[4] P. D. Bartlett, G. S. Hammond and K. Kwart, *Faraday Soc. Disc.*, **2**, 342 (1947).

[5] J. L. Kice, THIS JOURNAL, **76**, 6274 (1954).

[6] M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954); THIS JOURNAL, **77**, 1949 (1955).

his help. 2,3-Dichloronaphthoquinone was obtained from Naugatuck Co., and 2-*t*-butylanthraquinone was supplied by Dr. S. D. Ross from Sprague Electric Co. Methoxybenzoquinone and monochlorobenzoquinone were prepared according to methods described in references 7 and 8, respectively.

Each quinone was purified before the use, either by crystallization, or by high vacuum sublimation, the sharpness of the melting point being taken as the criterion of purity. All the reactions were carried out in toluene solution at 65°. Toluene was used as a solvent and not isoöctane (the latter solvent was used in previous investigations), since the solubility of many quinones in isoöctane was too low. A typical experiment was carried out with 10 cc. of a solution containing 0.1–0.5 mmole of acetyl peroxide and the required amount of quinone. Such a solution was deaerated by the conventional freezing and thawing procedure, sealed off in a flask, which then was heated for two hours in a constant temperature bath. At the end of this period, the flask was removed from the bath, the reaction interrupted by cooling its contents to $-80°$, and finally the contents were analyzed for CH_4, CO_2 and C_2H_6 formed in the process.[9] Under these conditions, about 5% of peroxide is decomposed.

Results

All the experimental results are summarized in Table I. The third column of this table gives the ratio CH_4/CO_2 formed in each experiment, while the CH_4/CO_2 ratio obtained in experiments carried out in absence of a quinone was found to be 0.73. The values of k_{II}/k_I are computed from the equation derived in the introductory part of this paper. It should be noted that the ratios of rate constants k_{II}/k_I remain essentially constant, even if the mole per cent. of a quinone present in a solution is varied by a factor of 4. This observation is considered as a justification of the assumed kinetic scheme.

It is assumed implicitly in our mechanism that one methyl radical reacts with one molecule of a quinone. Such an assumption is plausible if only a small fraction of quinone reacts with methyl radicals. The lowest initial concentration of the most reactive quinone was about 5×10^{-3} mmole/cc., and at this concentration about $^1/_5$ of generated methyl radicals were reacting with the quinone. Since the amount of methyl radicals generated per cc. did not exceed 3×10^{-3} mmole, it follows that not more than 12% of quinone was consumed in the reaction.

The unimolecular rate constants of acetyl peroxide decomposition were computed on the basis of CO_2 formed. Their constancy indicates that the presence of a quinone does not affect the rate of the unimolecular decomposition of acetyl peroxide, *i.e.*, quinone does not react *directly* with acetyl peroxide.

Discussion

The results given in Table I are averaged and recalculated in two ways. The second column of Table II lists the values of the respective methyl affinities of quinones, *i.e.*, the k_{II} values computed on the basis of $k_{II} = 1$ for benzene, while the third column lists them in units in which $k_{II} = 1$ for *p*-benzoquinone. Inspection of Table II leads to the following conclusions:

1. The reactivity of quinones decreases rapidly along the series 1,4-benzoquinone, 1,4-naphthoquinone, 1,4-anthraquinone. The reactivity of the latter compound could not be measured, since its solubility is too low. It may be assumed, however, that its reactivity is approximately identical with that of 2-*t*-butylanthraquinone.

It seems that this decrease in reactivity reflects the decrease in the "olefinic" character of the respective C=C double bonds.

2. The 1,2-quinones are less reactive than the respective 1,4-quinones.

3. The substitution of a hydrogen atom by a methyl or methoxy group, *i.e.*, an electron donating group, decreases the reactivity of a quinone. On the other hand, the introduction of a chlorine atom (an electron-withdrawing group) seems to increase the reactivity of a quinone. The peculiar behavior of chloranil and of 2,3-dichloronaphthoquinone is discussed later.

It has been mentioned earlier in this paper that the structure of the primary addition product Q·R is still undetermined, and it is not clear whether the reacting radical attacks initially the O atom or the C=C double bond. We would like to suggest tentatively that our results indicate that it is the C=C double bond which is attacked initially by methyl radicals. It seems that whenever the C=C double bond is shielded by some groups or bulky atoms the reactivity of quinone decreases. Thus, in parabenzoquinone, both C=C double bonds are exposed, while in 1,4-naphthaquinone one of them is shielded, and in anthraquinone both of them are shielded. This increase in shielding is paralleled with a considerable decrease of reactivity. Similar observation is made when one compares the remarkable decrease in reactivity of duroquinone as compared with those of toluquinone and xyloquinone (notice that in the former compound both C=C double bonds are shielded by the four methyl groups). Similarly the comparison of the reactivity of 2,3-dimethylnaphthoquinone with reactivities of its isomers confirms again our hypothesis. However, the most remarkable demonstration of our rule is found in the series of chlorinated quinones. While a substitution of a hydrogen atom by chlorine *increases* the reactivity of a quinone, and the introduction of a second chlorine atom increases its reactivity still further, the reactivity of chloranil (a quinone in which both C=C double bonds are shielded by chlorine atoms) and of 2,3-dichloronapthoquinone is strikingly low.[10]

Another evidence favoring our hypothesis is found in the observation of Aparicio and Waters,[1c] who reported the 2,5-di-*t*-butylbenzoquinone to be extraordinarily unreactive. The bulky *t*-butyl groups shield effectively the C=C double bonds, and not the C=O bonds, as is suggested by the above investigators,[11] and thus the low reactivity of this quinone may be construed as evidence for the addition to the C=C double bonds.

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[7] H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909).

[8] R. M. Husband, C. D. Logan and C. B. Purves, *Can. J. Chem.*, **33**, 68 (1955).

[9] Details of analytical procedure are described in This Journal, **76**, 5981 (1954).

[10] It is strange, however, that the reactivity of chloranil and of 2,3-dichloronaphthoquinone are so extraordinarily low, and lower than the reactivity of respective methyl compounds.

[11] If a radical is added to the oxygen atom, then the free rotation around the C–O bond would be hindered by the presence of a bulky group. This does not lead necessarily to steric hindrance for the addition process.

The Intrinsic Reactivities of Radicals.—The reactivities of quinones toward styryl radicals and radicals derived from allyl acetate were determined by studying the inhibition of the respective polymerizations by quinones.[3–5] The results are summarized in Table III, which gives also, for the sake of comparison, the reactivities of the pertinent quinones toward methyl radicals. A plot of logarithms of the relative reactivities of styryl radicals toward various quinones *versus* logarithms of corresponding methyl affinities results in a straight line (see Fig. 1). A similar linear relationship was reported previously by Levy and Szwarc,[6] who compared the reactivities of methyl and trichloromethyl radicals toward various aromatic hydrocarbons.

Functional relations of this type are well known, and their meaning is as follows. Say that reagents A and B react with a series of substrates M_1, M_2, . . . M_i, . . .

$$A + M_i \longrightarrow \text{products}$$

or

$$B + M_j \longrightarrow \text{products}$$

and let us denote by E_{A_i} and E_{B_j} the respective activation energies and by S_{A_i} and S_{B_j} the respective entropies of activation. The existence of a linear type of relation, as discussed above, demands that S_{A_i} = const. independent of i, S_{B_j} = const. (on the whole different from the previous one) independent of j, and

$$\Delta E_{A_{ij}} = E_{A_i} - E_{A_j} = \alpha(E_{B_i} - E_{B_j}) = \alpha \times \Delta E_{B_{ij}}$$

where α is independent of i and j. The above relation is still preserved even if for some substrate, say M_n, S_{A_n} and S_{B_n} differ from the other respective entropies of activation, provided that the difference $S_{A_i} - S_{A_n} = S_{B_i} - S_{B_n}$.[12]

The slope of the straight line resulting from the above relation is identical of course with α and it was proposed[6] to consider it as a measure of the relative intrinsic reactivity of a radical. Thus, the results shown in Fig. 1 indicate the styryl radical to be 0.45 as reactive as the methyl radical. Taking the relative intrinsic reactivity of methyl radical as unity, we derive the following values for relative intrinsic reactivities of styryl and CCl_3 radicals

Radical	Relative intrinsic reactivity
CH_3	1.00
CCl_3	0.51 (ref. 6)
$\sim\!\!\sim CH_2 \cdot \dot{C}H \cdot C_6H_5$	0.45

It is necessary to point out at this stage that chloranil does not fit to the proposed relation. Its low reactivity toward methyl radicals has been discussed previously and its behavior was explained tentatively in terms of steric hindrance. On the other hand, Breitenbach[3] reported that chloranil is *more* reactive toward styryl radicals than *p*-benzoquinone and, similarly, Bartlett[4] found that radicals formed in the polymerization of allyl acetate react easier with chloranil than with *p*-benzoquinone. However, recent studies of inhibition by Kice[5] indicate that *p*-benzoquinone is a more powerful inhibitor in polymerization of methyl methacrylate than chloranil, the respective rate constants of addition being 2400 and 120 for benzoquinone and chloranil, respectively. It is possible that the peculiar behavior of chloranil results from its ability to copolymerize with the growing radical chain. Indeed, Kice[5] reports a considerable extent of copolymerization in the case of chloranil, and similar observation is reported by Bickel and Waters.[1b]

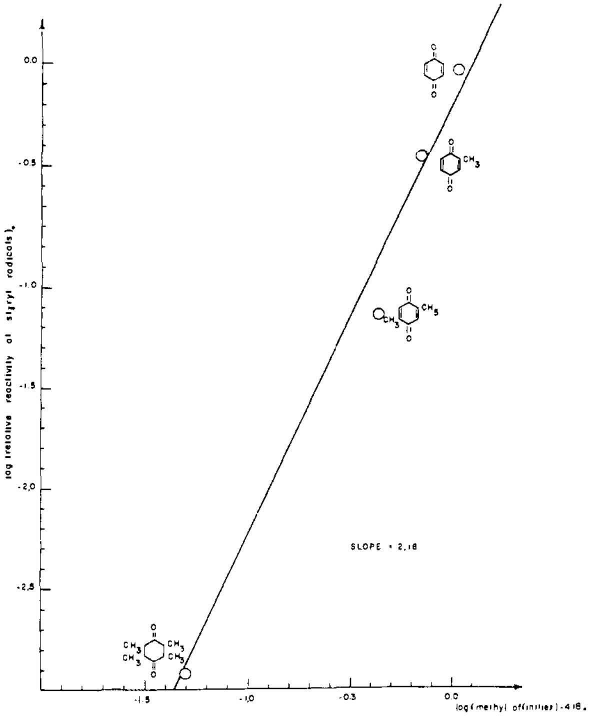

Fig. 1.

Reactivities and Oxidation–Reduction Potentials of Quinones.—There is no obvious reason why the oxidation–reduction potentials of quinones should parallel their reactivities toward radical, especially that the former entities are characteristic for an equilibrium, while the latter are related to a rate process. Nevertheless, comparing the oxidation–reduction potentials of quinones, determined in alcoholic solution by Fieser and his school,[13] with the corresponding methyl affinities reveals a monotonic relation between these entities (see Table II).

It was shown by Evans, Gergely and DeHeer[14] that for a series of non-substituted quinones the differences in oxidation–reduction potentials may be accounted for by the differences in the resonance energies of the respective quinones and quinols. Hence, our finding may suggest that the changes in the resonance energy of the system

$$Q + R \longrightarrow Q \cdot R$$

parallel the changes in the resonance energy of the system

$$Q + 2H \longrightarrow QH_2$$

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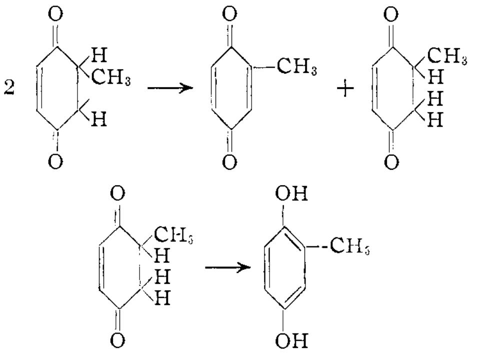
[12] For example, if the presence of some statistical factor g speeds up the reaction involving the substrate M_n, the linear relation discussed above is not upset, provided that the statistical factor g applies to the reaction with A as well as with B.

[13] L. F. Fieser, *et al.*, for survey see L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944.

[14] M. G. Evans, J. Gergely and J. DeHeer, *Trans. Faraday Soc.*, **42**, 113 (1946).

Products of Reaction.—It is assumed that $Q\cdot CH_3$ is the first product of the reaction involving a quinone and methyl radicals; however, $Q\cdot CH_3$ cannot be the final product of the reaction. The final product of the reaction must result from the interaction involving either two $Q\cdot CH_3$ species or $Q\cdot CH_3$ and iso-C_8H_{17} radicals. It seems improbable that $Q\cdot CH_3$ would react with another methyl radical since, if that were the case, then one would expect an increase in k_{II}/k_I for a decreasing X_Q, contrary to experimental findings.

Unsuccessful attempts were made to isolate and identify the final product of the reaction. The reaction with *p*-benzoquinone in isoöctane yields a purple compound, which precipitates on cooling the solvent to about −15°. This compound can be dissolved again in various solvents including water the solution, however, being yellow. On analysis, it is found however, that the compound contains "active" hydrogen, suggesting the presence of hydroxylic group. This might indicate the occurrence of reactions such as



or

$$Q\cdot CH_3 + \text{iso-}C_8H_{17} \longrightarrow Q\cdot H\cdot CH_3 + \textit{iso-}C_8H_{16}$$

In conclusion, we would like to thank the National Science Foundation for financial support of this research.

SYRACUSE, N. Y.

[CONTRIBUTION FROM THE CHEMICAL AND RADIOLOGICAL LABORATORIES]

Hydrogen Bonding of Phosphoryl Compounds with Chloroform and Other Solvents

BY ERNEST HALPERN, JAMES BOUCK, HAROLD FINEGOLD AND JEROME GOLDENSON

RECEIVED MARCH 10, 1955

The hydrogen bonding of $POCl_3$, $(C_2H_5O)_3PO$ and $(n\text{-}C_4H_9)_3PO$ with chloroform, pentachloroethane, *sym*-tetrachloroethane and *n*-heptane was studied by means of infrared spectroscopy. The order of hydrogen bonding of the phosphoryl compounds was as follows: $(n\text{-}C_4H_9)_3PO > (C_2H_5O)_3PO > POCl_3$. The order of hydrogen bonding of the solvents was: $CHCl_3 > CHCl_2\text{–}CCl_3 > CHCl_2\text{–}CHCl_2 >> n\text{-}C_7H_{16}$ (none).

Introduction

From a determination of the differences in the heat of mixing of chloroform with fifteen phosphoryl compounds, Kosolapoff and McCullough[1] found that hydrogen bonding is increased by replacement of groups attached to the phosphorus atom in the order of Cl < OR < R, and concluded that the hydrogen bonding ability is enhanced with increased electron density at the central group. Progressive increases in hydrogen bonding were shown as in the following series: $POCl_3 < ROP(O)Cl_2 < (RO_2)P(O)Cl < (RO)_3PO < RP(O)(OR')_2 < R_2P(O)(OR)$. Previous work on the hydrogen bonding of the C–H linkage is given in references 2 to 11.

In the work described in this paper, the association of phosphorus oxychloride, triethyl phosphate and tri-*n*-butyl phosphine oxide with chloroform, *sym*-tetrachloroethane, pentachloroethane and *n*-heptane was studied by means of infrared spectroscopy. Absorption bands due to the P=O and P–O–C (in the case of triethyl phosphate) linkages were investigated as well as the C–H linkage of the chloroform and other acceptor solvents. Evidence of association of the hydrogen bonding type was found with all the chlorinated acceptor solvents, but not with *n*-heptane. By determination of the changes in the integrated absorption intensities of the C–H band, the order of hydrogen bonding strengths of the acceptor solvents for phosphorus oxychloride, triethyl phosphate and tri-*n*-butyl phosphine oxide was found to be as follows: $CHCl_3 > CHCl_2\text{–}CCl_3 > CHCl_2\text{–}CHCl_2 \gg n\text{-}C_7H_{16}$ (none). The order of hydrogen bonding strengths of the phosphoryl compounds for the acceptor solvents was confirmed[1] to be as follows: $(n\text{-}C_4H_9)_3PO > (C_2H_5O)_3PO > POCl_3$.

Equipment.—A Perkin-Elmer model 12C equipped with a lithium fluoride prism was used to study the C–H absorption bands (fundamentals) of the acceptor solvents. A Perkin-Elmer model 21 with sodium chloride optics was used to study the P=O absorption band of the phosphoryl compounds.

Purification of Materials. $CHCl_3$.—Since the alcohol used as a stabilizer in chloroform would interfere with hydrogen bonding studies, it was removed by washing with water. The chloroform was then dried over calcium chloride and the infrared spectrum determined to ensure that the O–H absorption peak of the alcohol was removed.

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[1] G. M. Kosolapoff and J. F. McCullough, THIS JOURNAL, **73**, 5392 (1951).

[2] D. B. MacLeod and F. J. Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

[3] S. Glasstone, *ibid.*, **33**, 200 (1937).

[4] R. H. Ewell, *J. Chem. Phys.*, **5**, 967 (1937).

[5] W. Gordy, THIS JOURNAL, **60**, 605 (1938).

[6] A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938).

[7] M. J. Copley, G. F. Zellhoefer and C. S. Marvel, *ibid.*, **60**, 2666 (1938).

[8] W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

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