population, M_λ, may be quite small (10 to 20%), but some 20 to 50% of the total binding may occur in this structure, judging from the size of the overlap population, m_λ(a,b), in it. Furthermore, the total overlap population, m(a,b), is rather insensitive to λ, particularly in the range $\lambda = 0.3$ to 0.7.

The LiH results (Tables III and IV) show negative gross populations, M_λ, for the three Li$^-$H$^+$ structures. These are quite small, but far from negligible and their existence may be due either to the inadequacies of the wave functions themselves or to the approximate nature of the population analysis formulas. A similar, but rather smaller, effect is found in the MO population analysis.[2]

An interesting point about the LiH results is their similarity to those of H_2, particularly in the gross structure populations. In both cases, the covalent structure accounts for 87% of the total population. Conventional ideas would say that the ionic structures are more important in LiH which has a large dipole moment and ionic crystal.[14]

From the various overlap populations in LiH (Table IV), it seems that a substantial amount of the binding occurs in the ionic structures. The total overlap population in the molecule, 0.624, is quite similar to that found in other small molecules[2] and agrees with that (0.741) for LiH from the population analysis[15] of a MO wave function. The gross atomic populations also agree rather well with those found from the MO wave function,[15] and this suggests that despite the imperfections of the population analysis method, there is significant agreement in its results for both MO and valence bond wave functions.

Table IV reveals the expected small repulsions between the lithium 1s electrons and that of the hydrogen atom by the small negative values of the appropriate overlap populations. The total gross atomic populations, given in the last row of Table III, show the expected 2.00 electrons in the lithium 1s AOs. The lithium atom as a whole, however, has lost 0.27 electrons to the hydrogen atom. This over-all loss is made up of a loss of 0.50 electron from the 2sAO and a gain of 0.23 electron by the 2pσAO. More than this it is impossible to say without making further assumptions, since the amounts of promotion and charge transfer are formally inseparable. It has been suggested[2] that charge transfer be thought of as involving only the 2pσAO, and if this is so, we can describe the lithium atom as 50% promoted to the $(1s)^2(2s)(2p)$ configuration. This agrees well with Karo's results[3] from the population analysis of the LiH MO wave function in which configuration interaction is included.

The butadiene results (Table V) are rather as expected on classical ideas of resonance between valence bond structures. After the non-resonating structures, the long bonded structure is the most important contributor to the ground state wave function and this conclusion differs from that of Berry.[5] He rejected the wave function used here on the grounds that the ionic structures are underweighted in it, and this is a reasonable point of view since the basis functions of the 2p$_\pi$ AOs were represented by Slater AOs. Perhaps it would be valuable to repeat the calculations with SCF AOs for the 2p$_\pi$ basis functions, although there are some serious questions as to the behavior of the σ electrons in butadiene. For the present, it seems sufficient to say that the calculation based on Slater AOs does not contradict the classical ideas of resonance in butadiene.

Acknowledgments.—This work was carried out while the author was on leave of absence at the Department of Molecular Structure and Spectra, University of Chicago. The author is indebted to Professors R. S. Mulliken and F. A. Matsen for bringing the idea of structure populations to his notice and for much valuable advice during the course of the work. Some comments from a referee were also very helpful.

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The Validity of Frequency Shift-Enthalpy Correlations. I. Adducts of Phenol with Nitrogen and Oxygen Donors

BY MELVIN D. JOESTEN[1] AND RUSSELL S. DRAGO

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The correlation between frequency shift and enthalpy is tested by examining thermodynamic and infrared data for the interaction of phenol with thirty-three bases in carbon tetrachloride. Contrary to literature reports a plot of enthalpy *vs.* $\Delta\nu_{O-H}$ is linear for phenol adducts. The relationship holds within ±0.5 kcal./mole. The general equation derived for predicting enthalpy values for phenol–base association from frequency shift data is $-\Delta H$ (kcal./mole) $= 0.016\ \Delta\nu_{O-H} + 0.63$. The log K *vs.* $\Delta\nu_{O-H}$ relationship is found to be limited to similar bases where no unusual entropy effects are observed and where the entropy change is a linear function of the enthalpy.

Introduction

In 1937 Badger and Bauer[2] proposed that the shift in the infrared stretching frequency of a group, X–H, upon complexation to a base was linearly related to the enthalpy for hydrogen bond formation. Until recent years, there has been little reliable enthalpy work available to test this pro-

[1] U. S. Rubber Fellow, 1961–1962. Abstracted in part from the Ph.D. thesis of M. D. Joesten, University of Illinois (1962).

[2] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

posal. However, many workers have utilized the large number of equilibrium constants available to correlate infrared stretching frequency shifts, $\Delta\nu_s$, with aqueous acidity constants, pK_a, and nonaqueous association constants, $\log K_{\text{assn}}$. Gordon[3] has recently summarized the work in this area. A linear correlation of either pK_a or $\log K_{\text{assn}}$ with $\Delta\nu_s$ is obtained only for bases with similar structure. When no attempt is made to separate the bases into structurally similar groups, appreciable deviations occur, and the correlations have little value for predicting equilibrium constants.

On the basis of available enthalpy data for some phenol adducts, it was recently concluded[4] that "unhappily the data do not substantiate the proposed relation of Badger." Some of the enthalpy data utilized to draw this conclusion do not agree with results from our measurements. Re-evaluation of some systems reported in the literature, examination of selected new systems and utilization of some recently measured enthalpy data[5-8] leads us to conclude that the Badger–Bauer relationship is applicable for predicting enthalpy values for phenol adducts with a wide variety of oxygen and nitrogen bases. The attempted correlation of frequency shifts with equilibrium constants is not as successful.

Experimental

Materials.—The preparation and purification of the amides and the purification of phenol have been described earlier.[5] Mallinckrodt Analytical Reagent acetone was refluxed over Drierite for 24 hr. and then distilled twice at atmospheric pressure. Triethylamine was distilled from acetic anhydride, dried with activated alumina and then distilled twice at atmospheric pressure. Acetonitrile was shaken with a saturated KOH solution, decanted and dried over anhydrous sodium carbonate for 24 hr., and then distilled twice from P_2O_5 at atmospheric pressure. Trimethylphosphine oxide was prepared by the method of Burg and McKee.[9]

The trimethylphosphine oxide was sublimed at about 70° and 150 mm. pressure just before use in an experiment. Mallinckrodt Analytical Reagent ethyl acetate was refluxed over barium oxide for 12 hr. and distilled at atmospheric pressure.

Fisher Spectranalyzed carbon tetrachloride was used as the solvent in all studies except the triethylamine system. Fisher Spectranalyzed *n*-heptane was used for this donor.

Apparatus.—The apparatus used for thermodynamic measurements has been described previously.[5] The O–H stretching frequency shifts were measured on a Beckman Model IR-7 double-beam spectrometer with a fore-prism/grating optical system using a sodium chloride prism. The slit width at 3100 cm.$^{-1}$ was 0.37 mm. Sodium chloride cells of 0.2 mm. thickness were used.

Statistical Treatment of Data.—All errors are estimated at the 90% confidence level. For equilibrium constant determinations the sample variance[10] was calculated, and the error was determined by using the equation $M = X + ts/\sqrt{n}$. All terms are defined in the reported reference.[10]

The values for the molar absorptivity terms were also treated by the sample variance technique. Enthalpy values were calculated from the slope of the $\log K$ *vs.* $1/T$ curve. Regression analysis[10] was used to obtain the slope and its error limits. Entropy values were calculated from the equation $\Delta F^0 = \Delta H^0 - T\Delta S^0$.

Procedure.—A. Infrared Measurements.—Infrared spectra of 0.15 M solutions of phenol with sufficient base added to complex about 90% of the phenol were recorded. Since triethylamine reacts with carbon tetrachloride, the solution of phenol and triethylamine was prepared by adding triethylamine directly to phenol and then diluting with carbon tetrachloride so that the amount of free triethylamine could be kept at a minimum. The O–H shift is so great in the Et_3N-phenol system that there is considerable overlap of the complex peak with a phenol peak in the 3050 cm.$^{-1}$ region. The spectrum was resolved by subtracting the absorbance due to the free phenol in solution. The estimated error in $\Delta\nu_{O-H}$ for Et_3N—PhOH is ± 10 cm.$^{-1}$. The estimated error for all other bases is ± 3 cm.$^{-1}$.

B. Thermodynamic Measurements.—The general procedure used for making thermodynamic measurements has been described previously.[5] For a given system it is first necessary to determine whether the molar absorptivity term $\epsilon_c - \epsilon_A$ is temperature dependent. This is done by measuring absorbance differences ($A - A^0$) for three solutions at 25° and 35–40° and calculating $\epsilon_c - \epsilon_A$ at the two temperatures.[5] If $\epsilon_C - \epsilon_A$ is found to be constant within experimental error, the molar absorptivity term is assumed to be independent of temperature changes in this range. For DMTCA and DMMCA the temperature dependence and the amount of change in $\epsilon_C - \epsilon_A - \epsilon_D$ already have been discussed.[5,6] In this work the molar absorptivity term was found to be temperature dependent for the acetonitrile, acetone and ethyl acetate systems. In these cases a series of experiments were run to determine the extent of change in $\epsilon_C - \epsilon_A$.

After this was accomplished, absorbance differences were measured for a single solution at five or six temperatures. Then, the equilibrium constants were calculated at the various temperatures, and the enthalpy was obtained from a $\log K$ *vs.* $1/T$ plot.

Since the amount of change in $\epsilon_C - \epsilon_A$ with temperature is important for enthalpy determinations, a more detailed discussion of the procedure used to determine this change is necessary. The same procedure[5] used to calculate the equilibrium constant at 25° is repeated at two other temperatures within a 15° range. The resulting $\epsilon_C - \epsilon_A$ values are plotted *vs.* temperature to see if the change is linear. A linear decrease in $\epsilon_C - \epsilon_A$ with increase in temperature has been observed for all temperature-dependent molar absorptivity terms at 283 mμ over this temperature range. Once the change has been shown to be linear, further measurements are made at 25 and 35–40° to accurately determine the amount of change. Since $A - A^0$ values are taken for the same three solutions at both temperatures, errors introduced in solution preparation and transfer are reduced.

The measured value for the per cent. change in $\epsilon_C - \epsilon_A$/°C. remains constant for a given system even when the absolute values measured for $\epsilon_c - \epsilon_A$ at the two temperatures vary. The per cent. decreases in $\epsilon_C - \epsilon_A$/°C. with increase in temperature for the acetonitrile, acetone and ethyl acetate systems are 0.75%/°C., 1.4%/°C., and 0.9%/°C., respectively. The values for $\epsilon_C - \epsilon_A$ at 25° are: $\epsilon_C - \epsilon_A$ (283 mμ) for acetonitrile, 938 ± 34; $\epsilon_C - \epsilon_A - \epsilon_D$ (284 mμ) for acetone, 890 ± 70; and $\epsilon_C - \epsilon_A$(283.5 mμ) for ethyl acetate, 1010 ± 90.

Enthalpy values can be calculated from $A - A^0$ measurements for one solution at six different temperatures by using the values for the molar absorptivity terms together with their degree of change with temperature. The use of the extreme error limits of $\epsilon_C - \epsilon_A$ at 25° has little effect on the calculated enthalpy value. However, error in the per cent. change in $\epsilon_C - \epsilon_A$/°C. has a large effect.

The ethyl acetate system can be used to demonstrate the relative importance of errors in $\epsilon_C - \epsilon_A$ and in the per cent. change in $\epsilon_C - \epsilon_A$/°C. If $\epsilon_C - \epsilon_A(25°) = 900$ is used with the temperature correction of −0.9%/°C increase, an enthalpy value of −3.6 kcal./mole is obtained. When $\epsilon_C - \epsilon_A(25°) = 1000$ is used with the same temperature correction, the enthalpy is −3.5 kcal./mole. This demonstrates that the enthalpy values are fairly insensitive to the absolute value of $\epsilon_C - \epsilon_A$. However, if $\epsilon_C - \epsilon_A = 1000$ is used without the

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TABLE I[a]

FREQUENCY SHIFTS AND THERMODYNAMIC DATA FOR PHENOL–BASE ADDUCTS

	A. Base	$\Delta\nu_{O-H}$[b]	$-\Delta H^0$, kcal./mole	$-\Delta S_{25}$, e.u.	$\frac{\Delta S}{\Delta H}$	K_{25}, l. mole^{-1}	Ref.
1.	$(Me_3SiO)_4$	144	3.2				7
2.	EtOAc	164	3.2 ± 0.5	6.3 ± 1.6	1.97	9.3 ± 0.3	This work
3.	$Me_3SiOSiMe_3$	169	2.9				7
4.	$Cl_3C\overset{O}{C}NMe_2$	171	3.8 ± .5	5.8 ± 1.5	1.57	32 ± 3	6
5.	MeCN	178	3.2 ± .5	7.9 ± 1.6	2.39	5.0 ± 0.2	This work
6.	Me_2CO	193	3.3 ± .5	6.2 ± 1.2	1.88	13.5 ± 1.0	This work
7.	$Me_2SiCH_2CH_2SiMe_2O$	245	4.9				7
8.	$ClCH_2\overset{O}{C}NMe_2$	272	4.7 ± .5	8.5 ± 1.6	1.81	38 ± 2	5
9.	Et_2O	279	5.0				7
10.	$H\overset{O}{C}NMe_2$	294	6.1 ± .4	12.1 ± 1.0	1.98	64 ± 1	6
11.	$Et\overset{O}{C}NMe_2$	325	6.4 ± .2	12.1 ± .6	1.89	107 ± 2	6
12.	$(t\text{-}Bu)_2O$	329	5.9				7
13.	$Me\overset{O}{C}NMe_2$	342	6.4 ± .2	11.7 ± .6	1.83	134 ± 3	5
14.	Me_3PO	464	7.4 ± .5	10.2 ± 2.0	1.38	1480 ± 20	This work
15.	Et_3N	553	9.2 ± .1	21.7 ± 0.3	2.36	89 ± 4	This work
	B. Base	$\Delta\nu_{O-H}$	$-\Delta H^0$, kcal./mole	$-\Delta S_{25}$, e.u.	$\frac{\Delta S}{\Delta H}$	K_{20}, l. mole^{-1}	Ref.
16.	$Cl_3C\overset{O}{P}(OEt)_2$	260	3.1	1.84	0.59	73.2	8
17.	$F\overset{O}{P}Et_2$	270	5.0	8.1	1.62	82.5	8
18.	$Cl_2HC\overset{O}{P}(OEt)_2$	275	4.95	6.9	1.40	133.1	8
19.	$H\overset{O}{P}(OMe)_2$	300	5.3	8.3	1.56	123.1	8
20.	$F\overset{O}{P}(OEt)_2$	305	4.7	6.1	1.30	129.0	8
21.	$H\overset{O}{P}(OEt)_2$	310	4.7	5.7	1.20	161.9	8
22.	$(MeO)_3PO$	315	5.3	7.5	1.41	182.9	8
23.	$H\overset{O}{P}(OC_3H_7)_2$	320	5.2	6.95	1.34	199.7	8
24.	$CH_2Cl\overset{O}{P}(OEt)_2$	325	6.6	11.4	1.72	239.0	8
25.	$H\overset{O}{P}(OCHMe_2)_2$	330	5.45	7.35	1.35	237.3	8
26.	$Me\overset{O}{P}(OC_3H_6Cl)_2$	335	6.0	9.3	1.55	247.0	8
27.	$(EtO)_3PO$	345	6.7	10.9	1.63	350.5	8
28.	$Et\overset{O}{P}(OMe)_2$	355	6.0	8.7	1.45	329.7	8
29.	$Me\overset{O}{P}(OEt)_2$	360	6.3	9.4	1.50	381.0	8
30.	$Et_2N\overset{O}{P}(OEt)_2$	395	5.65	6.55	1.16	518.2	8
31.	Ph_3PO	430	6.7	8.7	1.30	1055	8
32.	Me_3PO	470	6.65	7.4	1.11	1836	8
33.	Et_3PO	510	6.8	7.3	1.18	2522	8
34.	C_5H_5N	465	7.5	17.2	2.29	64.0	8
35.	EtOAc	154	4.8	11.9	2.48	9.2	11

[a] Frequency shifts for 2, 4, 5, 6, 8, 10, 11, 13, 14, 15 were measured in this Laboratory according to the procedure described in the experimental section. [b] ν_{O-H} = 3609 cm.$^{-1}$.

temperature correction, an enthalpy value of −5.5 kcal. is obtained. Therefore, the temperature correction must be applied to the molar absorptivity term to obtain accurate enthalpy values.

In order to test the accuracy of making enthalpy measurements by measuring $A - A^0$ values for a single solution at different temperatures, an alternative procedure was also used for ethyl acetate. A solution of phenol was placed in the reference cell and a phenol–ethyl acetate solution of similar total phenol concentration in the sample cell. Absorbance differences ($A - A^0$) were measured at 283.5 mμ at four different temperatures. This procedure was repeated for two more solutions containing the same total phenol concentration but different concentrations of ethyl acetate. All three solutions were prepared from the same stock solutions of phenol and ethyl acetate just before use. Equilibrium constants were calculated from these measurements.[5] Twelve equilibrium constants at eight different

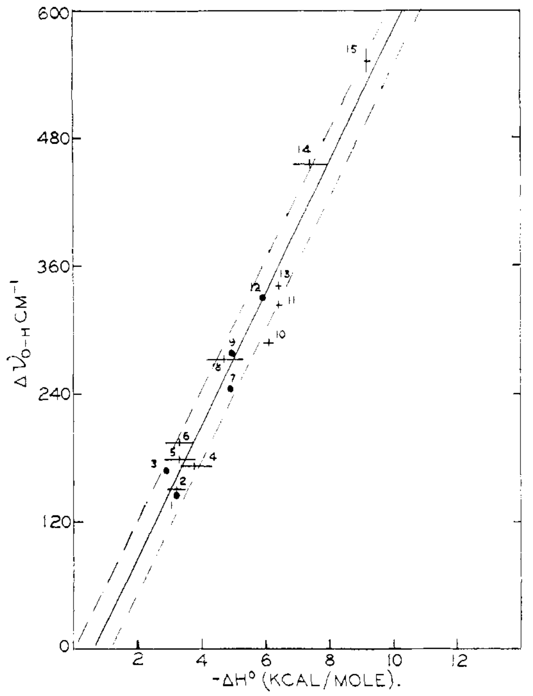

Fig. 1.—A plot of enthalpy *versus* $\Delta\nu_{O\text{-}H}$ for a series of phenol-base adducts. The bases are numbered according to their listing in Table I.

temperatures were obtained. An enthalpy value of -3.2 ± 0.8 kcal./mole was obtained from a least squares analysis of the data. This agrees very well with the value obtained by making measurements on a single solution.

The use of a single solution for enthalpy measurements offers many advantages, especially in systems where the molar absorptivity term is independent of temperature. Most reported enthalpy data are based on measurements of the equilibrium constant at only two or three temperatures. More accurate enthalpy values can be obtained from measurements on a single solution at several temperatures.

The molar absorptivity terms for the triethylamine and trimethylphosphine oxide systems were found to be independent of temperature. The values of $\epsilon_C - \epsilon_A$ obtained for these two systems are: $\epsilon_C - \epsilon_A$(282 mμ) for Et_3N in *n*-heptane, 1457 ± 32; and $\epsilon_C - \epsilon_A$(284 mμ) for Me_3PO, 1596 ± 10.

Results

A summary of the frequency shifts and thermodynamic data measured for several donor–phenol systems is contained in Table I.

Discussion

Fig. 1 is a least squares plot of $\Delta\nu_{O-H}$ *vs.* ΔH for the first fifteen bases listed in Table I. The estimated error is ± 0.5 kcal./mole at the 90% confidence level. In order to simplify Fig. 1 the bases listed in section B of Table I were not included. The enthalpy values reported for donors numbered 16, 30, 32, 33 and 35 fall outside the error limits of the curve. In the present study thermodynamic data and frequency shifts were remeasured for phenol adducts of trimethylphosphine oxide (32) and ethyl acetate (35). The resulting values which lie on the curve (Fig. 1) are listed in section A of Table I as bases 14 and 2, respectively.

If trimethylphosphine oxide is not freshly sublimed before each experiment, low enthalpy values are obtained. The deviation from the line in Fig. 1 of the data reported in the literature for compounds 16, 30 and 33 could be due to their hygroscopicity.

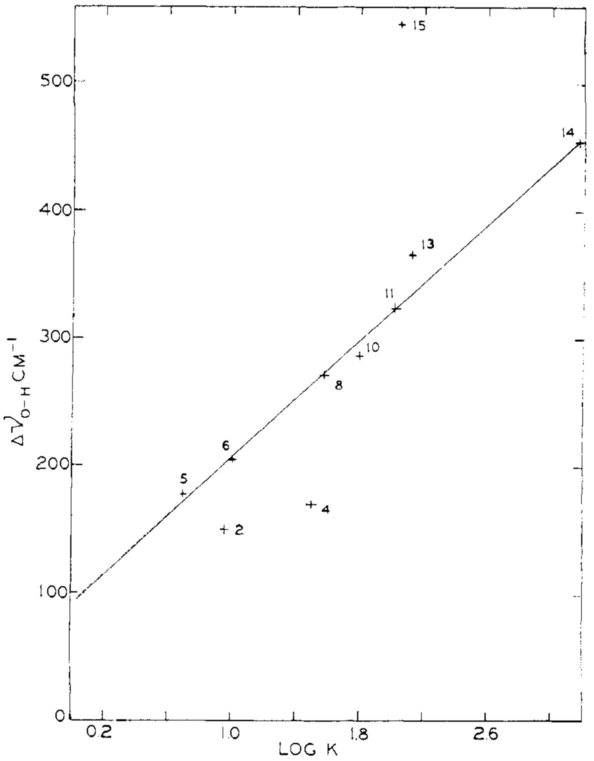

Fig. 2.—A plot of log *K versus* $\Delta\nu_{O\text{-}H}$ for a series of phenol-base adducts. The bases are numbered according to their listing in Table I.

A possible source of error in the reported data on ethyl acetate[11] could be the wave length selected for measurements. In previous work[11] measurements were made at 273, 278 and 280 mμ. Absorbance differences ($A - A^0$) are not significant at these wave lengths unless very large base concentrations (0.19 *M*) are used. Also, much larger error limits must be imposed on enthalpy data obtained from measurements on different solutions at only two or three temperatures (discussed in Experimental section).

It is concluded that a linear relationship exists between enthalpy and frequency shift for phenol–base adducts. The equation derived from a least squares analysis of the data for the first fifteen bases in Table I is

$$-\Delta H\,(\text{kcal./mole}) = 0.016\Delta\nu_{O-H} + 0.63 \quad (1)$$

Frequency shift data for phenol adducts are given in references 4, 12 and 13. Enthalpy values accurate to ± 0.5 kcal./mole can be predicted for phenol–base adducts by using available frequency shifts and equation (1).

Figure 2 is a plot of log *K vs.* $\Delta\nu_{O-H}$ for adducts of ten bases studied in this Laboratory. The predicted equilibrium constants for ethyl acetate, N,N-dimethyltrichloroacetamide (DMTCA), N,N-

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dimethylacetamide (DMA) and triethylamine are 3.3, 4.9, 251 and 9120, respectively. These values vary considerably from the experimentally determined values reported in Table I. This demonstrates the limited application of using a log *K vs.* $\Delta\nu_{O-H}$ relationship to predict equilibrium constants.

The $\Delta S/\Delta H$ ratios contained in Table I indicate that entropy effects are causing deviations in the log *K vs.* $\Delta\nu_{O-H}$ plot. The $\Delta S/\Delta H$ ratio is 1.8–2.0 for acetone and all amides except DMTCA. The unusual entropy effect in the case of DMTCA has been explained in a previous paper[6] as being evidence for the interaction of the chlorine *cis* to the carbonyl with phenol. For the nitrogen bases (acetonitrile, triethylamine, pyridine) the $\Delta S/\Delta H$ ratio is 2.3–2.4. The organophosphorus compounds have a larger range of values for $\Delta S/\Delta H$, but all are less than 1.7. Diethyltrichloromethylphosphonate $[Cl_3C\overset{O}{P}(OEt)_2]$ has a low value for the ratio $\Delta S/\Delta H$ in comparison with the other phosphorus compounds. Since this compound is similar in structure to DMTCA $(Cl_3C\overset{O}{C}NMe_2)$, we propose that the chlorine of the $-CCl_3$ group in diethyltrichloromethylphosphonate interacts with phenol as reported previously for DMTCA.[6] This chelate effect produces an entropy term favoring complexation and increases the equilibrium constant.

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[CONTRIBUTION NO. 1134 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH, PITTSBURGH 13, PENNSYLVANIA]

Destructive Autoxidation of Metal Chelates. III. Effects of Additives on the Reaction. Metal Acetylacetonates as Radical Sources[1]

BY EDWARD M. ARNETT[2] AND MORRIS A. MENDELSOHN[3]

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The autoxidative decomposition of Fe(III) acetylacetonate at 100° under pure oxygen in diphenyl ether as solvent is inhibited and slowed by benzoyl peroxide and strongly inhibited by azobisisobutyronitrile, both of which compounds usually serve as good autoxidation initiators. Conversely, the reaction is not inhibited by phenol, hydroquinone or 2,4,6-tri-*t*-butylphenol which are usually good antioxidants. N,N'-Diphenyl *p*-phenylenediamine is a fairly good inhibitor, but by far the most potent inhibiting action is produced by introducing ferrocene and the acetylacetonates of some other transition metals even though the latter chelates themselves are easily autoxidized. These results suggest that rather stable radicals are formed by thermal decomposition of the chelate and that these radicals are intercepted by the radicals produced from initiator decomposition but not by most inhibitors. It is found that the chelates which undergo facile autoxidation will initiate the polymerization of styrene.

In two previous papers[4,5] we have shown that various beta-diketone chelates decompose irreversibly in the presence of molecular oxygen at 100° in diphenyl ether as solvent.

The rate of this reaction depends to a considerable extent not only upon the structure of the organic ligand but also upon the ability of the metal to undergo valence changes. Both on the basis of the rate equation and the effect of variation of the structure of the ligand it appears likely that for the iron(III) beta-diketone chelates the organic part of the compound does not suffer direct initial attack in the reaction and that the decomposition does not occur through the complex chain reactions customary for autoxidation of hydrocarbon substrates.

In view of the conditions of the reaction and the nature of the products obtained, one would surely expect a free radical mechanism to be involved. We have therefore examined the influence of various free radical initiators and inhibitors on chelate autoxidation. It will be seen below that the effects produced by these compounds is unusual and that many of the chelates formed probably produce rather stable radicals, a supposition which is supported through the use of the same chelates to initiate and promote the polymerization of styrene.

It will be shown that not only do other organometallic compounds have a profound effect on the rate of chelate autoxidation but that mixtures of chelates frequently are insensitive to oxygen even though the component chelates are themselves quite easily oxidized.

Results

Initiators.—The rates of most kinds of autoxidation reactions are greatly affected by the presence of radical sources[6] such as benzoyl peroxide or azobisisobutyronitrile (AIBN) and indeed require some initiator for the commencement of reaction. In view of the very short or non-existent induction periods which we have usually observed for chelate

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[1] From the thesis of M. A. Mendelsohn submitted to the Department of Chemistry of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree in 1960.

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