

Table I. Infrared Spectra of Substituted Pentacarbonylchromium Compounds

	Ref	Solvent	Carbonyl stretching frequencies (cm <sup>-1</sup> )
(CO) <sub>5</sub> Cr=C(OCH <sub>3</sub> )CH <sub>3</sub> (1)		THF	2062 (m), 1980 (s), 1941 (vs)
[(CO) <sub>5</sub> CrC(OCH <sub>3</sub> )CH <sub>3</sub> ] <sup>-</sup> [(Ph <sub>3</sub> P) <sub>2</sub> N] <sup>+</sup> (3)		THF	2030 (w), 1937 (w), 1898 (vs), 1849 (s)
[(CO) <sub>5</sub> CrC(OCH <sub>3</sub> )CH <sub>3</sub> ] <sup>-</sup> Li <sup>+</sup>		THF	2030 (w), 1937 (w), 1898 (vs), 1848 (s)
[(CO) <sub>5</sub> CrI] <sup>-</sup> [(CH <sub>3</sub> CH <sub>2</sub> ) <sub>4</sub> N] <sup>+</sup>	a	KBr	2055 (w), 1930 (sh), 1914 (s), 1853 (m)
[(CO) <sub>5</sub> CrCOCH <sub>3</sub> ] <sup>-</sup> [(CH <sub>3</sub> ) <sub>4</sub> N] <sup>+</sup>	b	Nujol	2041 (s), 1883 (vs)
[(CO) <sub>5</sub> CrC(CF <sub>3</sub> )=CF(CF <sub>3</sub> )] <sup>-</sup> [(Ph <sub>3</sub> P) <sub>2</sub> N] <sup>+</sup>	7a	THF	2048 (w), 1920 (s), 1872 (m)

<sup>a</sup> E. W. Abel, I. S. Butler, and J. H. Reid, *J. Chem. Soc.*, 2068 (1963). <sup>b</sup> E. O. Fisher and A. Maasbol, *Chem. Ber.*, **100**, 2445 (1967).

(THF) at -78°. Treatment of this solution with excess DCl in diethyl ether gave monodeuterated carbene complex **1** (90% yield; 7.3% *d*<sub>0</sub>, 90.0% *d*<sub>1</sub>, 2.4% *d*<sub>2</sub>, 0.6% *d*<sub>3</sub> by mass spectrometry). In a separate experiment, treatment of a solution of **2** with 1 equiv of bis(triphenylphosphine)iminium chloride<sup>5</sup> in tetrahydrofuran followed by the addition of hexane resulted in the precipitation of a yellow (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> salt of the carbene anion (**3**) in 95% yield. Attempts to isolate lithium salt **2** have given pyrophoric residues; in contrast, the (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> salt (**3**) can be weighed in air, washed with water, and stored at 0° for several days with only slight decomposition.<sup>6,7</sup>

The nmr and ir spectra of **3** indicate that the structure is best described as the vinylpentacarbonylchromium anion **3b**. The nmr spectrum of **3** in tetrahydrofuran-*d*<sub>3</sub> contains two one-proton singlets at δ 3.78 and 4.52<sup>8</sup> due to the two nonequivalent vinyl hydrogens of **3b**, in addition to a methoxy singlet at δ 3.29 and a 30 H multiplet at δ 7.4–7.9 due to (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>. The nmr spectrum of **3** remains unchanged up to 120° where rapid decomposition ensues and indicates a substantial rotational barrier about the carbon-carbon bond of **3**. The carbonyl stretching frequencies of anion **3** are all shifted to substantially lower frequency than their counterparts in carbene complex **1** and are similar to those observed for other substituted pentacarbonylchromium anions (Table I).

The very intense and widely separated ir bands of carbene complex **1** at 1941 cm<sup>-1</sup> and of the carbene anion **3** at 1898 cm<sup>-1</sup> allow the determination of the relative abundances of **1** and **3** in solution and therefore provide a means of determining the acidity of **1** relative to common acids. THF solutions containing **3** and acids of varying strength were prepared at low temperature and the relative concentrations of carbene complex **1** and of the carbene anion **3** were measured at 0° by ir spectroscopy. The carbene complex **1** is remarkably acidic. Neither 10 equiv of CH<sub>3</sub>OH nor 10 equiv of diethyl malonate gave measurable protonation of **3**; 10 equiv of phenol gave a 30:70 ratio of **1**:**3** and 1 equiv of *p*-cyanophenol gave a 55:45 ratio of **1**:**3**. Thus, the thermodynamic acidity of **1** in THF is approximately the same as *p*-cyanophenol.

(5) J. K. Ruff, *Inorg. Syn.*, in press. We wish to thank Professor Ruff for a preprint describing the synthesis of (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>Cl<sup>-</sup>.

(6) Appreciable decomposition occurs within several days at room temperature and made analysis difficult. *Anal.* Calcd for C<sub>44</sub>H<sub>36</sub>NO<sub>6</sub>P<sub>2</sub>Cr: C, 67.07; H, 4.49; N, 1.77; P, 7.86; Cr, 6.60. Found: C, 64.72; H, 4.94; N, 1.61; P, 7.38; Cr, 5.80.

(7) The bis(triphenylphosphine)iminium cation has been used in the isolation of stable salts of several otherwise unstable transition metal-carbonyl anions: (a) W. J. Schlientz and J. K. Ruff, *J. Organometal. Chem.*, **33**, C64 (1971); (b) W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, **94**, 2516 (1972).

(8) For comparison, the two vinylic protons of the lithium enolate of *tert*-butyl acetate appear at δ 3.14 and 3.44 in benzene: M. W. Rathke and D. F. Sullivan, *J. Amer. Chem. Soc.*, **95**, 3050 (1973).

**1** is one of the most acidic neutral carbon acids known. The high acidity of **1** can be understood in terms of resonance form **1b** which draws attention to the analogy between alkylalkoxycarbene complexes and positively charged O-alkylated ketones. The high acidity of **1** can also be ascribed in part to the delocalization of negative charge onto the electronegative oxygen atoms of the pentacarbonylchromium moiety in **3b**.

The lithium salt of the carbene anion **2** is more easily protonated than the corresponding [(Ph<sub>3</sub>P)<sub>2</sub>N]<sup>+</sup> salt **3**. Thus, addition of 1 equiv of diethyl malonate to a freshly generated solution of lithium salt **2** gave a 65:35 mixture of **1**:**2** while addition of 10 equiv of methanol gave a 15:85 mixture of **1** and **2**. In the presence of 5 equiv of hexamethylphosphoric triamide (a reagent known for its ability to solvate Li<sup>+</sup>), the lithium salt **2** behaved similar to the (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> salt **3** and required *p*-cyanophenol to effect protonation. We attribute the different behavior of **2** and **3** to the stabilization of conjugate bases (methoxide, phenoxide) by lithium ion, which facilitates protonation of the carbene anion in its presence. The (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> cation cannot stabilize these conjugate bases by coordination. The nmr and ir spectra of **2** and **3** are identical except for absorptions due to the (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> cation; consequently, we believe that the carbene anion is solvent separated<sup>9</sup> and not affected by the counterion.

Since metal-carbene complexes can readily be converted to esters by oxidation reactions,<sup>10</sup> carbene anions are the synthetic equivalent of ester enolates. The carbene anions are only weakly basic in relation to ester enolates and can be generated under mild conditions. The synthetic utility of these weakly basic but reactive anions is under investigation.

**Acknowledgment.** The support of this research by the National Science Foundation (Grant GP-32160) is gratefully acknowledged.

(9) Lithium tetracarbonylcobaltate (-I) exists as a solvent separated ion pair in THF: W. F. Edgell, J. Lyford, II, A. Barbetta, and C. I. Jose, *J. Amer. Chem. Soc.*, **93**, 6403 (1971).

(10) C. P. Casey and T. J. Burkhardt, *J. Amer. Chem. Soc.*, **94**, 6543 (1972).

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### Neutral Hydrolysis of *p*-Nitrophenyl Dichloroacetate in Highly Aqueous *tert*-Butyl Alcohol. Effects due to Solvent Structural Integrity

Sir:

Esters such as *p*-nitrophenyl dichloroacetate (**1**), which are activated by strong electron withdrawal in the

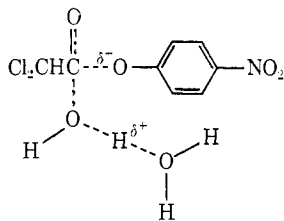


Figure 1.

acyl group, undergo hydrolysis at experimentally convenient rates through water-catalyzed nucleophilic attack at the carbonyl group by water.<sup>1-6</sup> Ample evidence has been provided for a transition state, represented pictorially in Figure 1, involving at least two water molecules, one of which acts as a proton transferring agent.<sup>7</sup> For **1**, no acid catalysis has been detected. The neutral hydrolysis of **1** by this mechanism could be exploited as a potentially useful model reaction for the study of effects due to varying diffusionaly averaged water structure<sup>8</sup> on rates of "water" reactions involving proton transfer. We report here rate constants for the hydrolysis of **1** in highly aqueous *tert*-butyl alcohol at slightly acidic pH values to suppress catalysis by OH<sup>-</sup>. Pertinent data are given in Table I.

Table I. Rate Constants ( $k_{\text{obsd}}$ )<sup>a</sup> and Activation Parameters<sup>b</sup> for the Hydrolysis of **1** at Various Mole Fractions of Water ( $n_{\text{H}_2\text{O}}$ ) in *tert*-Butyl Alcohol-H<sub>2</sub>O Containing 10<sup>-2</sup> *N* HCl (25 ± 0.05°)

$n_{\text{H}_2\text{O}}$	10 <sup>5</sup> $k_{\text{obsd}}$ , sec <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , eu
1.000	6020 <sup>c</sup>	9.2 ± 0.3	-33 ± 1
0.980	4120	7.4 ± 0.3	-40 ± 1
0.950	1770	5.5 ± 0.3	-48 ± 1
0.925	829	8.6 ± 0.2	-39 ± 1
0.900	561	10.7 ± 0.3	-33 ± 1
0.850	369	10.9 ± 0.3	-33 ± 1
0.800	303	10.9 ± 0.2	-32 ± 1
0.750	250	9.7 ± 0.4	-36 ± 1
0.700	210	10.4 ± 0.2	-36 ± 1

<sup>a</sup> Measured by the method given in ref 4; estimated error, 2%.

<sup>b</sup> Calculated from  $k_{\text{obsd}}$  values at 16.00, 20.00, 25.00, and 30.00°.

<sup>c</sup> In dilute buffer solutions with pH values ranging between at least 1.00 and 4.00, we find no significant variation of  $k_{\text{obsd}}$ .

Since solvolysis in pure *tert*-butyl alcohol is at least 10<sup>4</sup> times slower than in water, the rate constants pertain only for the "water" reactions. On lowering the mole fraction of water ( $n_{\text{H}_2\text{O}}$ ) from 1.000 to 0.700, the hydrolysis rate decreases smoothly. Earlier interpretations of rate retardations of a similar nature hinge mainly on the decreased availability of (free) water upon addition of the organic cosolvent.<sup>3,9</sup> Also from an electrostatic

(1) M. H. Palomäa, E. J. Salmi, and R. Korte, *Chem Ber.*, **72**, 790 (1939).

(2) A. Moffat and H. Hunt, *J. Amer. Chem. Soc.*, **81**, 2082 (1959).

(3) W. P. Jencks and J. Carriulo, *J. Amer. Chem. Soc.*, **83**, 1743 (1961).

(4) T. H. Fife and D. M. McMahon, *J. Amer. Chem. Soc.*, **91**, 7481 (1969).

(5) T. G. Bruice and S. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966.

(6) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, p 513.

(7) The strongly negative entropies of activation (-30 to -50 eu) associated with these types of mechanisms are indicative for immobilization of much more than two water molecules in the transition state.

(8) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, London, 1969.

(9) J. Koskikallio, *Acta Chem. Scand.*, **13**, 665 (1959).

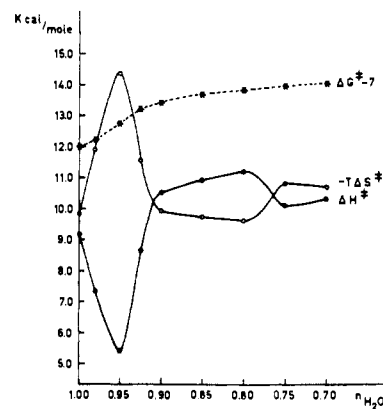


Figure 2. Plot of  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $-T\Delta S^\ddagger$  vs. mole fraction of H<sub>2</sub>O for the hydrolysis of **1** in *t*-BuOH-H<sub>2</sub>O at 25°.

viewpoint, a rate decrease might be expected because of destabilization of the polar transition state when the bulk dielectric constant is lowered. We find, however, that the actual situation is more complex than previously imagined. This is demonstrated dramatically by the behavior of the thermodynamic quantities of activation,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , as a function of solvent composition (Table I). Note that in pure water compared to  $n_{\text{H}_2\text{O}} = 0.900$  the contributions of  $-T\Delta S^\ddagger$  to  $\Delta G^\ddagger$  are equal and  $\Delta H^\ddagger$  changes by only 1.5 kcal mol<sup>-1</sup> but that there exists a nearly 9 kcal mol<sup>-1</sup> difference between  $\Delta H^\ddagger$  and  $-T\Delta S^\ddagger$  at  $n_{\text{H}_2\text{O}} = 0.950$ . The mirror image compensatory behavior of  $\Delta H^\ddagger$  and  $-T\Delta S^\ddagger$  is shown in Figure 2. Related phenomena (although less pronounced) have been reported by the schools of Winstein,<sup>10</sup> Arnett,<sup>11</sup> and Hyne<sup>12</sup> and by others<sup>13</sup> for nucleophilic displacement reactions not involving proton transfer (mainly S<sub>N</sub>1 solvolysis of *tert*-butyl chloride) in aqueous alcohols.<sup>14</sup> Several explanations have been offered for these observations, the most successful being couched in terms of substrate destabilization (decrease of  $\Delta H^\ddagger$ ) upon increase of long-range order in water induced by the organic cosolvent.<sup>11,13</sup> It is important to note that the positions of the extrema in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the hydrolysis of **1** (Table I) coincide approximately with the "magic" mole fraction for which striking low-angle X-ray scattering intensity peaks<sup>15a</sup> and maxima of excess ultrasound attenuation<sup>15b</sup> have been found.<sup>16</sup> Therefore, our results suggest that  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for hydrolysis of activated esters respond to, or may even be dominated by, changes in microheterogeneity in highly aqueous *tert*-butyl alcohol. Apparently, hydrolysis of **1** will be accompanied by a greater loss in entropy when water molecules of enhanced

(10) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, **79**, 5937 (1957).

(11) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Dugleby, *J. Amer. Chem. Soc.*, **87**, 1541 (1965).

(12) J. B. Hyne and R. Wills, *J. Amer. Chem. Soc.*, **85**, 3650 (1963).

(13) R. Huq, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1195 (1973), and references cited therein.

(14) "Water structure" effects on the dynamic basicity of water have also been suggested: (a) F. Hibbert and F. A. Long, *J. Amer. Chem. Soc.*, **94**, 7637 (1972); (b) L. Menninga and J. B. F. N. Engberts, *J. Phys. Chem.*, **77**, 1271 (1973).

(15) (a) F. Franks, "Water, a Comprehensive Treatise," Vol. 2, F. Franks, Ed., Plenum Press, New York, N. Y., 1973, Chapter 1; H. D. Bale, R. E. Shepler, and D. K. Sorger, *Phys. Chem. Liquids*, **1**, 181 (1968); (b) M. J. Blandamar, ref 15a, Chapter 9.

(16) Property extrema and enthalpy-entropy compensation behavior have been reviewed: R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).

structuredness<sup>17</sup> are involved in the transition state. The more favorable enthalpy due to increased hydrogen bonding under these conditions can only partly compensate the entropic loss. In the  $n_{H_2O}$  region from 0.900 to 0.700 long-range order is rapidly destroyed as reflected in rates of hydrolysis which are now slowed down through rather smooth changes in  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ .

Our findings may well have biochemical implications of some generality, since it has long been recognized that "water structure" may be either appreciably increased or decreased (compared to pure water) around the active sites of enzymes.<sup>18</sup> One of the consequences will be that for water-dependent enzymic processes involving hydrolysis of activated esters or mechanistically related reactions, there may occur a strong interdependence of *substituent effects* in the substrate and *solvent effects* due to changes in "water structure." Therefore, substituent effects obtained with the aid of suitable model reactions<sup>19</sup> in water may be substantially modified at the active site.

In the light of the present results we are encouraged to believe that the effect of "water structure" and its concomitant influence on thermodynamic parameters will become part of all theories for processes in aqueous solutions. However, at the moment complete separation of these effects from other influences and quantitative predictions must await further development in our understanding of the peculiar nature of water.<sup>20</sup>

Further studies of reactions which respond to perturbation of the structuredness of aqueous media are in progress.

(17) We leave open the question whether or not the enhanced structuredness is the one characteristic of pure water.

(18) H. J. C. Berendsen, "Theoretical and Experimental Biophysics," A. Cole, Ed., Marcel Dekker, New York, N. Y., 1967, p 1.

(19) For excellent reviews, see ref 5 and 6. We find that the ratio of  $k_{obsd}$  values for the hydrolysis of **1** and *p*-methoxyphenyl dichloroacetate changes from 22 in pure water to 43 at  $n_{H_2O} = 0.950$  in aqueous *tert*-butyl alcohol (30°C).

(20) Important theories have been developed recently: (a) A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **57**, 1281 (1972); (b) O. Weres and S. A. Rice, *J. Amer. Chem. Soc.*, **94**, 8983 (1972); (c) A. T. Hagler, H. A. Scheraga, and G. Némethy, *J. Phys. Chem.*, **76**, 3229 (1972).

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## A 2,2'-Bipyridine Derivative of Diiron Nonacarbonyl, $Fe_2(CO)_7dipy$ . Some Observations on the Nature and Function of Semibridging Carbonyl Groups

Sir:

Simple substitution products of the iron carbonyls in which the substituents are organic amines are previously unreported,<sup>1,2</sup> although  $Fe(CO)_4NH_3$  has been described.<sup>3</sup> We have found that use of THF as solvent for reactions of  $Fe_2(CO)_9$  allows the isolation of a number of unusual products not otherwise obtainable, in-

(1) Cf. F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience-Wiley, New York, N. Y., 1968, p 127.

(2) Studies by Hieber and coworkers found that direct reactions between the iron carbonyls and amines yield only disproportionation products, *i.e.*, salts containing amine-coordinated ferrous ion and carbonylate anions. Cf. W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2075, 2085 (1959), and earlier work cited there.

(3) W. Hieber and H. Beutner, *Z. Anorg. Allg. Chem.*, **317**, 63 (1962).

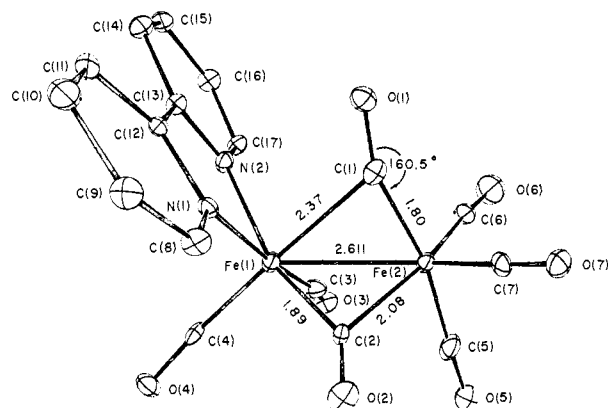


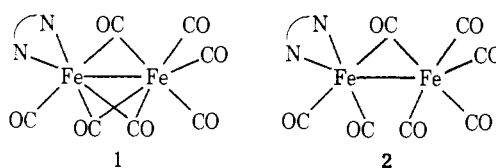
Figure 1. The structure of  $Fe_2(CO)_7dipy$ . The ellipsoids representing amplitudes of thermal vibration enclose 50% of the electron density. An atom numbering scheme is indicated.

cluding novel olefin complexes<sup>4</sup> and  $Fe(CO)_4py$ .<sup>5</sup> Another product readily obtained is  $Fe_2(CO)_7dipy$ , a red-purple, crystalline solid. We have characterized this compound fully by X-ray crystallography.<sup>6</sup> The structure is shown in Figure 1.

The structural features of greatest interest are the presence of only *one* ordinary bridging CO group (moderately unsymmetrical) and the occurrence of one grossly unsymmetrical carbonyl bridge.<sup>7</sup>

While the compound can be regarded as a substitution product of  $Fe_2(CO)_9$ , in contradistinction to being the result of a disproportion or other scission process, there has been an extensive rearrangement of the structure. The nature and significance of the rearrangement have been analyzed yielding important new insight into the principles governing the structures of metal carbonyls.

Mere substitution of two *cis* terminal CO groups by *dipy* would have afforded a structure of type **1**. We suggest that whether or not it is an actual intermediate this could not be stable relative to **2**, for the following reason.



Bridging CO groups are most likely much less efficient  $\pi$ -acids than terminal CO groups, and with the replacement of two terminal CO groups by *dipy*, a good  $\sigma$ -donor but a poor (compared to CO)  $\pi$ -acid, there is need to generate  $\pi$ -acid capacity among the remaining ligands. This is done by opening two CO bridges thereby creating two more terminal CO ligands and affording a structure of type **2**.<sup>9</sup>

(4) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **95**, 3798 (1973).

(5) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, in press.

(6) See paragraph at end of paper regarding supplementary material.

(7) As in  $(\eta^5-C_5H_5)_2V_2(CO)_8$  there is an ir band ( $\sim 1850\text{ cm}^{-1}$ ) between the normal ranges for bridge and terminal CO groups assignable to the grossly unsymmetrical one; this indicates that this structure persists in solution.

(8) F. A. Cotton, L. Kruczynski, and B. A. Frenz, *J. Amer. Chem. Soc.*, **95**, 951 (1973).

(9) This can be regarded as a simple substitution product of an initially singly bridged structure such as has been proposed for  $Os_2(CO)_6$ .<sup>10</sup> A  $(OC)_4Fe(\mu-CO)Fe(CO)_4$  structure is probably only a few kilocalories less stable than the  $(OC)_3Fe(\mu-CO)_2Fe(CO)_3$  for  $Fe_2(CO)_8$ .

(10) J. R. Moss and W. A. G. Graham, *Chem. Commun.*, 835 (1970).