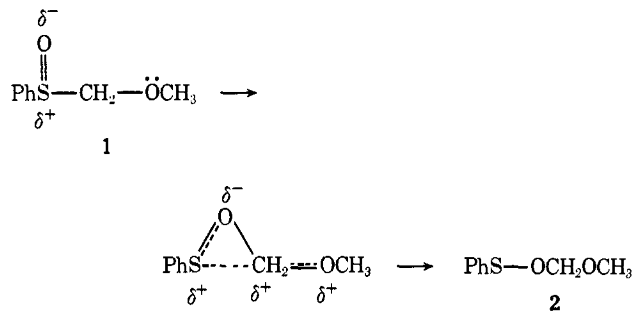
rearrange. These results suggest that **1** rearranges through a polarized activated complex (**5**), because



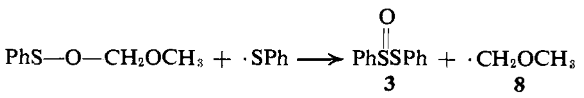
protonation of or hydrogen bonding with the sulfoxide oxygen should reduce its nucleophilicity. Further supporting evidence is the facilitation of rearrangement by the electron-releasing methoxyl group compared with the reluctance of the benzoyloxy-substituted sulfoxide to react below 110°.

Acids had just the opposite effect on the decomposition of **2** by acting as a catalyst, increasing the rate with stronger acids, and affording different products. Hydroquinone, however, was too weak an acid to catalyze the decomposition of **2**, but instead had a dramatic inhibitory effect on **2** (about 20% decomposition in 1 month at 36°). Hydroquinone also retarded the rearrangement of **1**. Whether hydroquinone inhibits the reactions of **1** by hydrogen bonding or of **1** and **2** by free-radical quenching can be considered.[15]

We found no significant change in the hydroquinone concentration (5 mol %) during the retarded rearrangement of **1** to **2** until an appreciable amount of **2** was formed (50%, 1 week). The slow decomposition of **2** was paralleled by a decrease in the hydroquinone nmr absorption with a concomitant appearance of the absorption peak of benzoquinone. Hydroquinone did not significantly change the product composition because of its low concentration.

The product composition and inhibitory effect of hydroquinone suggest that **2** decomposes by a free-radical chain mechanism. It is plausible that initiation occurs by homolytic cleavage of the S–O bond of **2** to give the thiophenoxyl (**6**) and methoxymethoxyl (**7**) radicals. Each of these conceivably could initiate a chain process by reacting with **2**. The following sequence is one in which **6** and methoxymethyl (**8**) radicals are chain carriers. The alternative involvement of **7** is unlikely, as it would require an unprecedented free-radical displacement reaction at carbon.

$$\underset{\mathbf{2}}{\mathrm{PhS{-}\vdots{-}OCH_2OCH_3}} \longrightarrow \underset{\mathbf{6}}{\mathrm{PhS\cdot}} + \underset{\mathbf{7}}{\mathrm{\cdot OCH_2OCH_3}}$$



$$\mathrm{PhS{-}O{-}CH_2OCH_3} + \mathrm{\cdot SPh} \longrightarrow \underset{\mathbf{3}}{\mathrm{Ph\overset{O}{\overset{\|}{S}}SPh}} + \underset{\mathbf{8}}{\mathrm{\cdot CH_2OCH_3}}$$

$$\mathrm{PhS{-}O{-}CH_2OCH_3} + \mathrm{\cdot CH_2OCH_3} \longrightarrow \mathrm{PhS\cdot} + \underset{\mathbf{4}}{\mathrm{CH_3OCH_2OCH_2OCH_3}}$$

The sensitivity of **2** to acids is not surprising, as it is an acetal of formaldehyde. What is at first surprising is again the formation of **3** as the major product. The formation of **3** in the acid-catalyzed reaction could be explained by the intermediacy of benzenesulfenic acid through a general scheme proposed by Kice and Cleveland.[16] The fate of the methoxymethyl group is complex.

Acknowledgments. This investigation was supported in part by a Frederick Gardner Cottrell grant from Research Corporation and a National Science Foundation Institutional Undergraduate Research grant.

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[15] A radical pair has been implicated in benzyl migration in the Meisenheimer rearrangement of amine oxides.[2c,d]

[16] J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **92**, 4757 (1970).

[17] National Science Foundation Undergraduate Research Participant, 1970.

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X-Ray Photoelectron Spectroscopy of Some Nickel Dithiolate Complexes

Sir:

The remarkable oxidation–reduction behavior of metal dithiolate compounds $[M(S_2C_2R_2)_n]^z$, where M is a large variety of transition metals, n is generally 2 or 3, R is CF_3, CN, C_6H_5, H, CH_3, etc., and z is 0, -1, or -2 (and sometimes -3 when n is 3), has generated an intense interest in the synthetic and theoretical aspects of these compounds.[1] In particular, the theoretical descriptions[2–4] of the nickel compounds have variously described the oxidation state of nickel in $[Ni(S_2C_2R_2)_2]$ as 0, +2, and +4. Because of the square stereochemistry about nickel, the zero oxidation state was considered unreasonable. The paramagnetic species $[Ni(S_2C_2R_2)_2]^-$ has been described as Ni(I) and Ni(III) and as indeterminate in the usual oxidation state formalism. There has been agreement that $[Ni(S_2C_2R_2)_2]^{2-}$ is best described as Ni(II) with two dianionic ligands.

X-Ray photoelectron spectroscopy[5] affords a unique opportunity for a fresh insight into this fairly complex bonding system, since both the metal and sulfur binding energies can easily be measured and the "formal" oxidation states determined.

We have obtained the nickel 2p $^3/_2$ and sulfur 2p binding energies for a series of nickel dithiolate compounds, $\{Ni[S_2C_2(C_6H_5)_2]_2\}^{0,-1,-2}$ and $\{Ni[S_2C_2(CN)_2]_2\}^{-1,-2}$, and some other pertinent materials by measurement with a Varian IEE-15 electron spectrometer. The samples were run as powders dusted onto cellophane tape. Air-sensitive samples were loaded in a glove bag under nitrogen. In the case of elemental nickel, it was necessary to sputter clean the powder with Ar^+ to remove the surface oxides. To compensate for sample charging, the spectra were referenced to the Au (4f $^7/_2$) electrons (E_b = 83.0 eV) from gold which was vacuum deposited onto each sample. The results re-

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[1] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[2] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

[3] S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *ibid.*, **86**, 4594 (1964).

[4] G. N. Schrauzer and V. P. Mayweg, *ibid.*, **87**, 3585 (1965).

[5] K. Siegbahn, *et al.*, "ESCA: Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, Sweden, 1967.

Table I. Nickel (2p $^3/_2$) and Sulfur (2p $^1/_2$, $^3/_2$) Binding Energies in Some Nickel Dithiolate and Other Compounds

Substance	Binding energy, eV Ni(2p $^3/_2$)	S(2p $^1/_2$, $^3/_2$)	FWHH, eV[a] Ni	S
Ni	852.8 (1)		2.0	
$Ni[(C_6H_5)_2PCH_2CH_2P(C_6H_5)(C_2H_5)](CO)_2$[b]	852.9 (1)		2.4	
$Ni[S_2C_2(C_6H_5)_2]_2$[c]	852.9 (1)	161.1 (1)	2.2	2.6
$[(C_2H_5)_4N]\{Ni[S_2C_2(C_6H_5)_2]_2\}$[d]	852.5 (1)	160.8 (1)	2.0	2.5
$(N_2H_5)_2\{Ni[S_2C_2(C_6H_5)_2]_2\}$[c]	852.8 (1)	160.5 (1)	2.0	2.4
$[(C_2H_5)_4N]\{Ni[S_2C_2(CN)_2]_2\}$[d]	853.1 (1)	161.3 (2)	2.0	2.5
$[(C_2H_5)_4N]_2\{Ni[S_2C_2(CN)_2]_2\}$[e]	853.1 (1)	161.4 (1)	1.8	2.2
$Na_2S_2C_2(CN)_2$[f]		161.4 (1)		2.6
$K_2Ni(CN)_3$[g]	854.7 (1)		2.0	
$Ni(CN)_2$	856.3 (1)		2.4	
$K_2Ni(CN)_4$	855.6 (2)		2.1	
NiO	856.2 (1)		4.2[h]	

[a] Full peak width at half-height. [b] Reference 6. [c] G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 1463 (1965). [d] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963). [e] J. F. Weiker, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, **86**, 4329 (1964). [f] G. Bähr and Schleitzer, *Chem. Ber.*, **90**, 438 (1957). [g] J. W. Eastes and W. M. Burgess, *J. Amer. Chem. Soc.*, **64**, 1187 (1942). [h] Broadening is due to satellites generated by multielectron processes.

ported in Table I are the average of at least three replicate measurements with the confidence limits taken as the standard deviations. The peak widths at half-height average 2.3 eV for nickel and 2.4 eV for sulfur. The individual values are given in Table I.

The carbon (1s) binding energies were not determined, because of the number of kinds of carbons in the compounds, as well as possible extraneous carbon impurities, which would make assignment of the chelate ring carbon energies very difficult.

It can be seen that the nickel binding energies in the three compounds, $\{Ni[S_2C_2(C_6H_5)_2]_2\}^{0,-1,-2}$, are very similar, *viz.*, 852.9, 852.5, and 852.8 eV, respectively. The cyano compounds, $\{Ni[S_2C_2(CN)_2]_2\}^{-1,-2}$, have the identical nickel binding energy, 853.1 eV, which is likewise about the same as that for the phenyl compounds and also for zerovalent nickel powder (852.8 eV) and the zerovalent nickel carbonyl derivative, $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)(C_2H_5)]\ Ni(CO)_2$[6] (852.9 eV). As expected, a nickel(I) compound, $K_2Ni(CN)_3$, has a higher binding energy (854.7 eV), and some nickel(II) compounds have considerably higher energies: NiO, 856.2 eV; $K_2Ni(CN)_4$, 855.6 eV; and $Ni(CN)_2$, 856.3 eV. It would therefore appear that Gray's description of the electronic structure of these compounds as having an indeterminate charge on nickel with the electrons encompassing the whole π-bonding system would be the closest approximation to these experimental results, although none of the previous theories seriously considered Ni(0) for these compounds.

If the increased electronic charge in going from the neutral compound to the -1 and -2 anions does not reside mainly on the nickel, it was of interest to observe the change in 2p binding energy of sulfur in these compounds. The 2p binding energy of sulfur[5] varies from 167.7 eV in SO_4^{2-} ($+6$) to 160.8 eV in S^{2-} (-2) in a linear fashion, or about 0.86 eV per unit oxidation state change.

If most of the charge on each one-electron reduction would reside mainly in molecular orbitals of the four equivalent sulfurs, each sulfur would change by only $-^1/_4$ charge, which is equivalent to a decrease in S(2p) binding energy of 0.21 eV. This is roughly twice the experimental error and is therefore just on the limit of significance. However, it is interesting to note that the trend is in the right direction for the three compounds, $\{Ni[S_2C_2(C_6H_5)_2]_2\}^{0,-1,-2}$, which have sulfur 2p binding energies of 161.1, 160.8, and 160.5 eV, respectively. This effect is not seen in the cyano compounds, however, where some charge could be more effectively removed by the cyano groups. Also the values of 160.8 and 160.5 eV for sulfur in the anionic phenyl compounds are nearly as low as that for Na_2S, and lower than that of $Na_2S_2C_2(CN)_2$, which indicates an unusually large charge density on sulfur.

In summary, these data indicate that the nickel dithiolate compounds are best assigned a formal oxidation state of zero for nickel with the additional charge on reduction going into molecular orbitals mainly residing on the ligands. Additional compounds of this type are being investigated.

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[6] This compound was donated by John Del Gaudio, University of Maryland.

Reaction of Ammonia Gas with Crystalline Substituted Benzoic Anhydrides

Sir:

An earlier communication reported[1] that single crystals of benzoic acids react anisotropically with gaseous ammonia and low boiling amines to form 1:1 salts in quantitative yield. However, the reaction of benzoic acid with ammonia in aqueous solution is known to be very fast[2] and its ready occurrence in the solid state leaves open the question of the generality of such reactions.

We now report that reactions of crystalline *p*-chloro- (**1**) and *p*-bromobenzoic anhydride (**2**) with ammonia gas occur in the solid state and may be faster than the reactions of the corresponding carboxylic acids with ammonia under comparable conditions. When platelets of the anhydride **1** are placed under a microscope in an enclosure through which is passed a stream of ammonia gas, a rapid change at the sides of the crystal is observed while the top face remains clear. The region of disorder then spreads as in the reactions of ammonia with benzoic acids. In Figure 1 is shown a succession of photographs of a crystal of **1** [lying on

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(1) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, **93**, 2784 (1971).

(2) The rate constant for the reaction of benzoic acid with water has been found to be 10^6 l. mol^{-1} sec^{-1} and the constant for the reaction with ammonia in aqueous solution could reasonably be assumed to lie between that value and 10^{11} l. mol^{-1} sec^{-1} (see E. F. Caldin, "Fast Reactions in Solution," Wiley, New York, N. Y., 1964, p 262 ff; E. Grunwald, *Progr. Phys. Org. Chem.*, **3**, 317 (1965)).