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

	Binding energy, eV		FWHH, eV[a]	
Substance	Ni(2p $^3/_2$)	S(2p $^1/_2$, $^3/_2$)	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)).

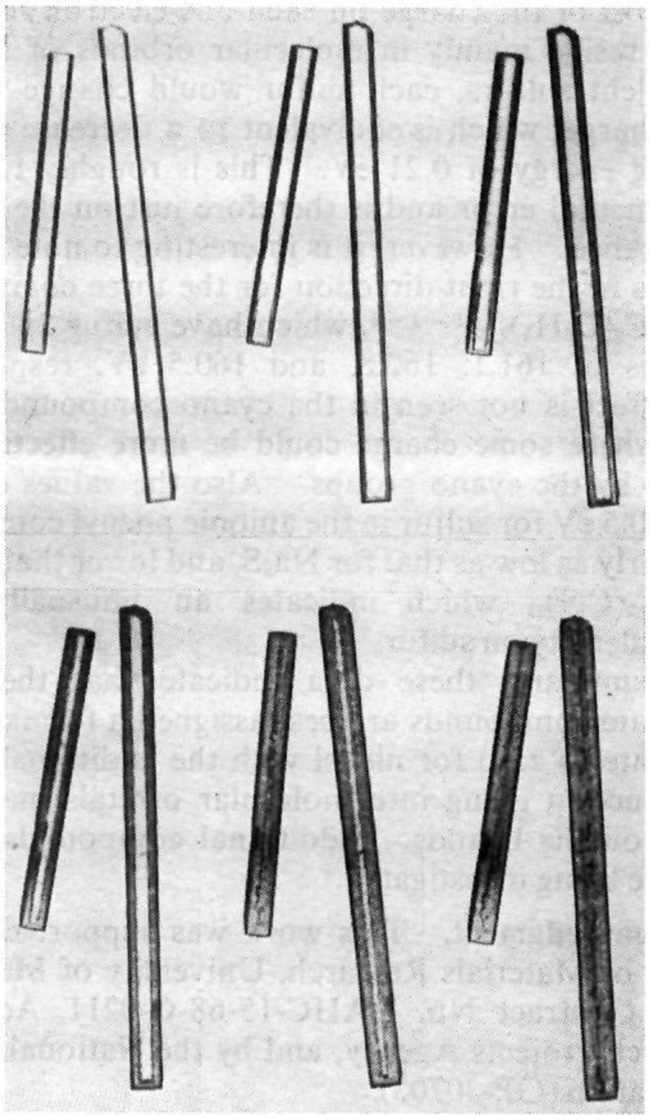

Figure 1. Reaction of crystals of *p*-chlorobenzoic anhydride with ammonia. The larger crystal is 1.1 × 0.07 mm. Times are from the upper left and proceeding from left to right: 0, 57, 195 min; second row, 300 min, 540 min, 24 hr.

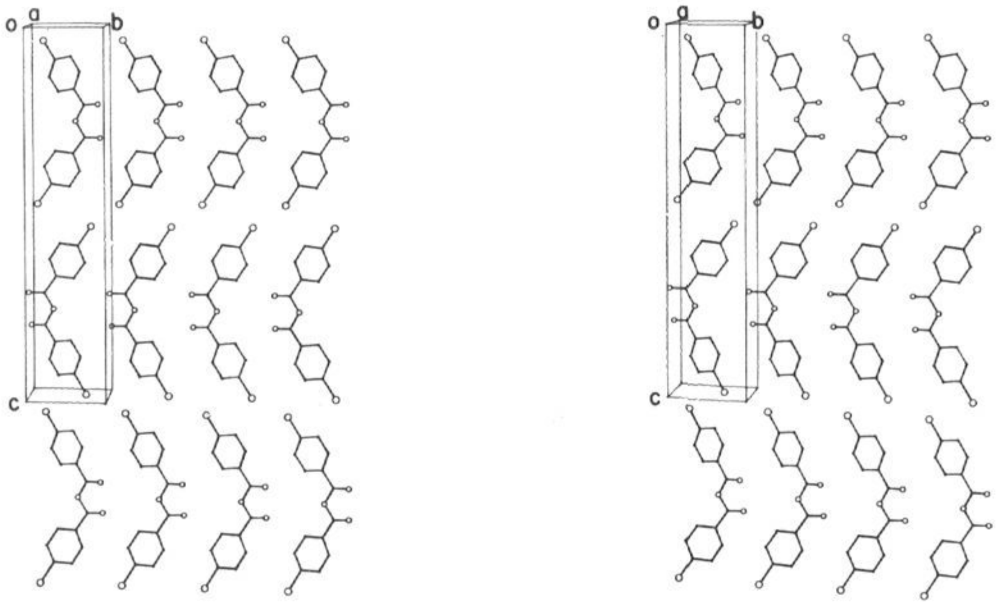

Figure 2. Stereopair view of the crystal structure of *p*-chlorobenzoic anhydride (data taken from ref 4). The face shown in Figure 1 corresponds to the 0*ab* face in this figure.

(001)] taken as reaction proceeds. The bromo anhydride **2** showed similar behavior. In each case the product "crystal" [3] gave a microanalysis correct for the expected 1:1 mixture of *p*-halobenzamide and ammonium *p*-halobenzoate.

Determinations of the crystal structures of *p*-chlorobenzoic anhydride[4] (Figure 2) and *p*-bromobenzoic anhydride[5] have shown that they are layered in the same fashion as the benzoic acids whose reactions with ammonia have been studied.[1] The top face (Figure 2) made up of *p*-halobenzene rings has remained clear while reaction of the ammonia occurs from the sides of the crystal where the carbonyl groups are more accessible as was observed with the acids.

The similarity in rates of the reactions of ammonia with crystalline *p*-halobenzoic anhydrides and those with the corresponding crystalline acids is striking. No data are available for the rates of reaction of ammonia in solution but the rate of reaction of *p*-chlorobenzoic anhydride in 75% dioxane–25% water at 58.25° has been found[6] to be 3.9 × 10^{-5} sec^{-1} which means that in solution the acid reacts with water (proton exchange) some 10^{11} times as fast as the anhydride reacts (hydrolysis). Ammonia must react with the acid in solution at a rate which is many orders of magnitude greater than with the anhydride. The fact that the rates are nearly equal in the solid–gas reaction taken in conjunction with the behavior observed through the microscope (Figure 1) provides strong evidence that the rate-limiting process is the loosening of the product layer in order to permit access of the ammonia to the next layer of substrate.

In a given single crystal the *p*-bromoanhydride (space group *C*2) has molecules of only one chirality. A single crystal of the bromo compound might react with an enantiomorphous amine such as 2-butylamine vapor in such a way as to favor one mirror image over the other. Single crystals of sufficient size to test this hypothesis have not yet been obtained. The reaction of bromine vapor with a finely powdered single crystal of 4,4′-dimethylchalcone (**3**) has been reported[7] to give the dibromide with an optical activity of about 6% of that shown by the fully resolved product.

We have also examined the reaction of single crystals of *trans*-stilbene with chlorine gas. In solution there was obtained, as shown by nmr analysis, a mixture of *dl*- and *meso*-stilbene dichlorides in a ratio of 2:1 in

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(3) Although the shape of the original crystal was retained, the product was a microcrystalline aggregate.

(4) M. Calleri, G. Ferraris, and D. Viterbo, *Atti Accad. Sci. Torino, Cl. Sci. Fis. Mat. Natur.*, **100**, 145 (1966).

(5) C. S. McCammon and J. Trotter, *Acta Crystallogr.*, **17**, 1333 (1964).

(6) E. Berliner and L. H. Altschul, *J. Amer. Chem. Soc.*, **74**, 4110 (1952).

(7) K. Penzien and G. M. J. Schmidt, *Angew. Chem.*, **81**, 628 (1969). When we allowed a single crystal of **3** to react with bromine vapor at room temperature on a microscope stage, however, it was observed to collapse to a puddle of melt after a few minutes. This reaction appears to deserve further investigation.

agreement with previous work.[8] However, the gas–solid reaction gave, after 30% conversion, a dichloride of which the nmr spectrum showed the *dl* but no detectable amount of the meso isomer.[9] Production exclusively of the *dl* isomer could result from the rigid environment which may constrain both chlorines to attack the double bond from the same side. Gas–solid reactions may have utility in increasing stereoselectivity in cases of this kind.

Acknowledgment. This research was supported by the Advanced Research Projects Agency.

[8] R. E. Buckles and D. F. Knaack, *J. Org. Chem.*, **25**, 20 (1960).

[9] The reaction of *trans*-stilbene is complicated by the appearance of a coating of what seems to be melt in a thin layer on the upper surface. This hardens as reaction proceeds from the sides of the crystal and no general melting occurs. Inspection of the crystal structure of *trans*-stilbene [J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), *Ser. A*, **162**, 568 (1937)] shows the molecules to be oriented much more nearly parallel to the most developed (001) face of the crystal. The best planes of the two nonequivalent molecules of *trans*-stilbene are inclined 41 and 43° to that face, whereas the average angle of the two CC(—O)═O planes with the major crystal face is 90° for the *p*-bromo anhydride and 71° for the *p*-chloro anhydride.

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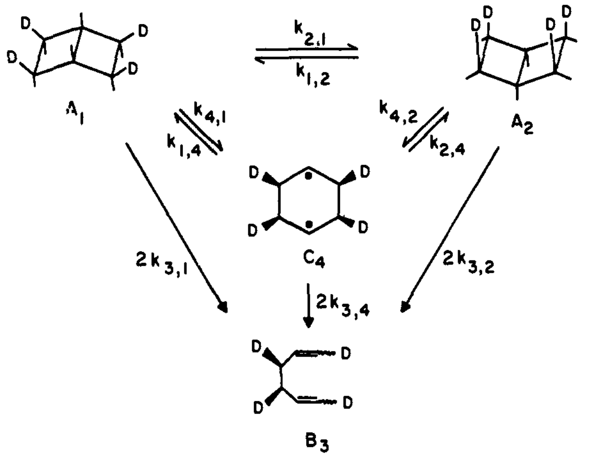
Inversion and Stereospecific Cleavage of Bicyclo[2.2.0]hexane[1]

Sir:

With few exceptions, the kinetic analysis of small hydrocarbon ring pyrolyses has either assumed or else deduced the intercession of a steady-state intermediate—the singlet biradical.[2–4] The relevant stereochemical facts are considerably more varied.[5]

We here report: (a) the discovery of the thermal inversion of bicyclo[2.2.0]-*exo-2,3,5,6-d*$_4$ ($A_1 \rightarrow A_2$, Figure 1),[6] (b) an unbiased kinetic analysis of competition between this process and cleavage to 1,5-hexadiene-*1,3,4,6-d*$_4$, and (c) the deduction of exclusively[7] stereospecific cleavage, fully in accord with predictions based upon naive considerations of orbital symmetry.[8]



$$\lambda_{cle} = k_{4,1}(1 - f_{ret}) + 2k_{3,1}$$
$$\lambda_{i+c} = k_{4,1} + 2k_{3,1} + 2k_{2,1}$$
$$f_{ret} = k_{1,4}/(k_{1,4} + k_{3,4})$$

Figure 1. Competitive cleavage and inversion of bicyclo[2.2.0]-hexane-*d*$_4$.

A_1 was prepared by an obvious variant of the van Tamelen synthesis[9] and its stereochemical assignment verified by pmr.[10] Two experimental first-order rate constants—those of cleavage (λ_{cle}) and of inversion plus cleavage (λ_{i+c})—were obtained at each of five temperatures by minimizing the sums of squares of the deviations (between calculated and observed areas) in five characteristic regions of the pmr spectra.[11] Concordant, but independently fitted values of the corresponding pairs of activation parameters (19 samples, t = 135–180°, $P \approx 450$ Torr) are listed in column 1 of Table I.[12,13] The pmr spectra of reactant–product mixtures were indistinguishable[7] from the superposition of those of their gc-purified components. Activation parameters for cleavage agree with the original report (footnote *d*, Table I); rate constants are trivially lower.

In order to avoid mechanistic bias, Figure 1 includes both the concerted and the biradical options. The detailed structure of the biradical (C_4) is not specified beyond its all-cis deuterium assignment. No doubt but that only the subtlest structural changes distinguish it from the transition states of the two alternative concerted processes of mechanistic rate constants $k_{2,1}$ and $k_{3,1}$. A reader who prefers the biradical option need only set $k_{21} = k_{31} = 0$ and consider column 2 of Table I.

[1] Taken in part from the Ph.D. Thesis of M.S. Benzon, Cornell University, 1971.

[2] The most notable exceptions are pyrolyses of sterically unencumbered cyclobutenes.[3]

[3] For exhaustive reviews, *cf.* (a) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); (b) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, **No. 21**, 14 (1970); (c) H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970).

[4] Typical examples are provided by L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); R. G. Bergman and W. L. Carter *ibid.*, **91**, 7411 (1969).

[5] (a) P. D. Bartlett, *Pure Appl. Chem.*, **27**, 597 (1971), and references cited therein; (b) H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 3935, 4884 (1961); (c) G. L. Closs and P. E. Pfeffer, *ibid.*, **90**, 2452 (1968); (d) J. E. Baldwin and P. W. Ford, *ibid.*, **91**, 7192 (1969); (e) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (f) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970); (g) J. A. Berson, W. Bauer, and M. M. Campbell, *ibid.*, **92**, 7515 (1970); (h) L. A. Paquette and G. L. Thompson, *ibid.*, **93**, 4920 (1971).

[6] Inversion of methylbicyclo[2.1.0]pentanes is long known: M. J. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962); J. P. Chesick, *ibid.*, **84**, 3250 (1962).

[7] Except where stated otherwise, such terms denote agreement between observed and anticipated values to within <2%.

[8] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[9] E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *J. Amer. Chem. Soc.*, **92**, 6092 (1971); R. N. McDonald and C. E. Reinecke, *J. Org. Chem.*, **32**, 1878 (1967).

[10] The overlapping multiplets of the undeuterated hydrocarbon simplify to a broadened singlet (τ 7.22) and a sharp doublet (τ 7.95, $J \sim 1$ Hz) in the expected 1:2 ratio; *cf.* S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 2870 (1963); R. Steinmetz, W. Hartmann, and G. O. Schenck, *Chem. Ber.*, **98**, 3854 (1965); K. B. Wiberg and D. E. Barth, *J. Amer. Chem. Soc.*, **91**, 5124 (1969), and references cited therein.

[11] τ 3.83–4.50 (C-2,5 of diene), 4.75–5.21 (C-1,6 of diene), 6.98–7.35 (C-1,4 of bicyclohexane), 7.35–7.70 (exo C-2,3,5,6 of bicyclohexane), 7.70–8.16 (endo C-2,3,5,6 of bicyclohexane + C-3,4 of diene).

[12] Copies of the algebraic analysis, experimental data, graphical summaries, and the FORTRAN program were made available to the editor and referees of this paper.

[13] For previous reports of bicyclo[2.2.0]hexane cleavage kinetics, *cf.* (a) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, **86**, 679 (1964); (b) R. Srinivasan, *Int. J. Chem. Kinet.*, **1**, 133 (1969); for those of substituted derivatives *cf.* (c) E. N. Cain, *Tetrahedron Lett.*, 1865 (1971); (d) E. N. Cain and R. K. Solly, *Int. J. Chem. Kinetic.*, **4**, 159 (1972).