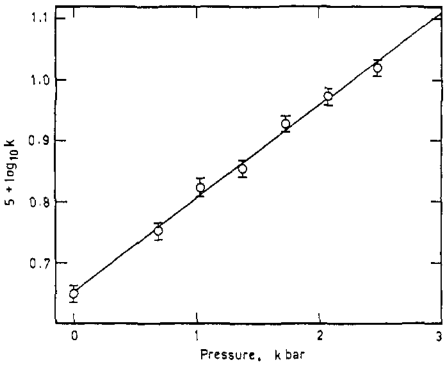

Figure 1. Pressure dependence of the first-order rate coefficient $k$ (sec$^{-1}$) for the exchange of all six waters of $Cr(H_2O)_6^{3+}$; the error bars represent ±3% uncertainty in $k$.

are evidently of the order of 1 cm$^3$ mol$^{-1}$. The observed $\Delta V^*$ for the hexaaquochromium(III) water exchange is therefore about 8 cm$^3$ mol$^{-1}$ more negative than can be explained on the basis of associative bond forming alone. We suggest that the main contribution to $\Delta V^*$ in the chromium(III)-water exchange originates in the vacancy created when the incoming water molecule is transferred to the first coordination sphere; the core complexes $Cr(H_2O)_6{}^{3+}$ and $Cr(H_2O)_7{}^{3+}$ can be regarded as being essentially spheres of the same effective radius ($r_{Cr^{3+}} + 2r_{H_2O}$).

The high degree of linearity of Figure 1 is unusual and merits comment. Hunt and Taube[9] point out that, because the compressibility of bulk water is large ($8.0 \times 10^{-4}$ cm$^3$ bar$^{-1}$ mol$^{-1}$ at 45° and 1 bar) compared with that of the first coordination sphere of a tripositive cationic complex, $\Delta V^*$ should be strongly pressure dependent for a water exchange process which involves equilibrium between solvent water and coordinated water, such as the associative (A) mechanism

$$H_2O + [\{Cr(H_2O)_6\}(H_2O)_x]^{3+} \overset{\text{fast}}{\rightleftharpoons} [\{Cr(H_2O)_6\}(H_2O)_{x+1}]^{3+} \quad (3)$$

$$[\{Cr(H_2O)_6\}(H_2O)_{x+1}]^{3+} \overset{\text{slow}}{\rightleftharpoons} [\{Cr(H_2O)_7\}(H_2O)_x]^{3+} \quad (4)$$

Here, the lifetime of the seven-coordinate complex is long relative to the time for exchange of the $x$ labile waters of the presumed second coordination sphere (solvation sheath) with bulk solvent and, because this complex is more compacted and therefore even less compressible than $[\{Cr(H_2O)_6\}(H_2O)_x]^{3+}$, $(\partial\Delta V^*/\partial P)_T$ would be slightly greater than $+8.0 \times 10^{-4}$ cm$^3$ bar$^{-1}$ mol$^{-1}$. The observation that $|(\partial\Delta V^*/\partial P)_T| < 2.0 \times 10^{-4}$ cm$^3$ bar$^{-1}$ mol$^{-1}$ is therefore difficult to reconcile with an A mechanism, but is consistent with an associative interchange ($I_a$) mechanism in which only the relatively incompressible solvated aquo complexes, and *not* bulk water, are directly involved in the activation process.

$$[\{Cr(H_2O)_6\}(H_2O)_x]^{3+} \longrightarrow [\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+*} \quad (5)$$

The lifetime of seven-coordination in (5) is short even relative to the time for exchange of the labile $(H_2O)_x$ with bulk solvent, and $[\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+}$ may exist only momentarily as the transition state. In this $I_a$ model, the major contributor to $\Delta V^*$ is presumably the collapse of part of the solvation sheath when one of its $x$ water molecules is transferred to the first coordination sphere.

The present data, combined with those of Hunt and Plane[7] for similar concentrations but lower temperatures, give $\Delta H^* = 26.2 \pm 0.3$ kcal mol$^{-1}$ and, for the exchange of *one* of the six coordinated water molecules by a *first-order* process (*i.e.*, ignoring the concentration of bulk water), $k'(25.0°) = 4.3 \times 10^{-7}$ sec$^{-1}$ and $\Delta S^* = +0.3 \pm 1.0$ cal deg$^{-1}$ mol$^{-1}$, at atmospheric pressure. This near-zero value of $\Delta S^*$ is consistent with the above view of the reaction mechanism as involving only modest relocations of water molecules within an independent $[\{Cr(H_2O)_6\}(H_2O)_x]^{3+}$ entity; the transition state $[\{Cr(H_2O)_7\}(H_2O)_{x-1}]^{3+}$ need not be significantly more or less ordered than the initial state.

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making and breaking to $\Delta V^*$ could be zero or even positive. Thus, in the absence of electrostriction effects, a small, positive $\Delta V^*$ in a reaction such as (2) is not necessarily indicative of a dissociative mechanism, but a negative $\Delta V^*$ is strong evidence for an associative process.

(11) On leave with the University of Adelaide until Aug 1971.

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## Reaction of Ammonia Gas with Crystalline Benzoic and Related Acids

*Sir:*

Although there have been scattered reports of reactions believed to have occurred between a molecular crystalline solid and a gas[1] there appears to have been no detailed study of such a reaction. We have now found that benzoic acid and a number of related carboxylic acids react, either as powders or as single crystals, with ammonia gas at 1 atm to give 1:1 ammonium salts. In each case, the product "crystal" is opaque but retains approximately the external shape of the crystal from which it was formed and in general has greater mechanical strength (resistance to crumbling) than the original crystal. Microanalysis of the product without any purification whatever gives carbon, hydrogen, and nitrogen values within 0.3% of the theoretical for the 1:1 salt. This gas–solid reaction is undoubtedly the method of choice for the preparation of many 1:1 ammonium salts.

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(1) (a) H. Morawetz, "Physics and Chemistry of the Organic Solid State," Vol. I, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience, New York, N. Y., 1963, p 313 ff. Other references not mentioned there include the following: (b) H. Morawetz, *Science*, **152**, 705 (1966); (c) C. Graebe and C. Liebermann, *Ann. Suppl.*, 7, 257 (1870); "Beilsteins Handbuch der Organische Chemie," Vol. 5, Springer-Verlag, Berlin, 1922, p 661; (d) P. Pfeiffer, O. Angern, L. Wang, R. Seydel, and K. Quehl, *J. Prakt. Chem.*, [2] **126**, 97 (1930); (e) R. E. Buckles, E. A. Hausman, and N. G. Wheeler, *J. Amer. Chem. Soc.*, **72**, 2494 (1950); (f) R. E. Buckles, W. E. Steinmetz, and N. G. Wheeler, *ibid.*, **72**, 2496 (1950); (g) M. M. Labes and H. W. Blakeslee, *J. Org. Chem.*, **32**, 1277 (1967); (h) D. Y. Curtin and A. R. Stein, *Can. J. Chem.*, **47**, 3637 (1969); (i) G. Friedman, M. Lahav, and G. M. J. Schmidt, *Israel J. Chem.*, 7, 191p (1969); (j) K. Penzien and G. M. J. Schmidt, *Angew. Chem.*, **81**, 628 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 608 (1969); (k) E. A. Meyers, E. J. Warwas, and C. K. Hancock, *J. Amer. Chem. Soc.*, **89**, 3565 (1967).

Table I. Physical and Crystal Properties of Benzoic and Related Acids

| | Mp, °C | $10^5 K_a$ | Space group | Most Prominent face | $a$, Å | $b$, Å | $c$, Å | $\alpha$, deg | $\beta$, deg | $\gamma$, deg | Vol/dimer, Å$^3$ | Calcd % vol increase on reaction |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acid | | | | | | | | | | | | |
| Benzoic[a,b] | 122 | 6.3[c] | $P2_1/c$ | (001) | 5.52 | 5.14 | 21.90 | 90 | 97 | 90 | 308 | |
| *p*-Chlorobenzoic[d,e] | 243 | 10.4[c] | $P\bar{1}$ | (100) | 14.190 | 6.213 | 3.852 | 91.25 | 95.32 | 92.93 | 338 | |
| *p*-Nitrobenzoic[f,g] | 241 | 37.6[c] | $C2/c$ | (100) | 21.43 | 5.07 | 12.97 | 90 | 96.4 | 90 | 350 | |
| α-*trans*-Cinnamic[h,i] | 133 | 3.7[c] | $P2_1/n$ | (010) | 7.79 | 18.07 | 5.67 | 90 | 97 | 90 | 396 | |
| 2-Naphthoic[j] | 185 | 6.9[c] | $P2_1/n$ | (100) | 30.59 | 5.00 | 5.63 | 90 | 92.6 | 90 | 430 | |
| (1:2) Ammonium acid salts | | | | | | | | | | | | |
| Benzoic[k] | | | $C2/c$ | (100) | 29.35 | 3.97 | 11.43 | 90 | 95.3 | 90 | 332 | 8 |
| *p*-Chlorobenzoic[l] | | | $C2/c$ | | 32.8 | 3.88 | 11.44 | 90 | 93 | 90 | 363 | 8 |
| *p*-Nitrobenzoic[m] | | | $P\bar{1}$ | (100) | 17.20 | 4.05 | 11.44 | 93.8 | 104.1 | 90.5 | 396 | *m* |
| *trans*-Cinnamic[n] | | | $I2/a$ | (100) | 37.87 | 5.84 | 7.62 | 90 | 95.5 | 90 | 419 | 6 |

[a] G. A. Sim, J. M. Robertson, and T. H. Goodwin, *Acta Crystallogr.*, **8**, 157 (1955). [b] Reference 2, pp 456–457. [c] N. A. Lang, "Handbook of Chemistry," 10th ed, McGraw-Hill, New York, N. Y., 1961, p 1198 ff. [d] J. Toussaint, *Acta Crystallogr.*, **4**, 71 (1951); J. M. Pollock and I. Woodward, *ibid.*, **7**, 605 (1954). [e] Reference 2, pp 466–467. [f] T. D. Sakore and L. M. Pant, *Acta Crystallogr.*, **21**, 715 (1966). [g] Reference 2, pp 477–478. [h] G. M. J. Schmidt, *J. Chem. Soc.*, 2014 (1964). [i] Reference 2, p 615. [j] J. Trotter, *Acta Crystallogr.*, **14**, 101 (1961); J. Krc, Jr., and R. Hinch, Jr., *Anal. Chem.*, **26**, 780 (1954). [k] This investigation; compare J. M. Skinner, G. M. D. Stewart, and J. C. Speakman, *J. Chem. Soc.*, 180 (1954). [l] H. H. Mills and J. C. Speakman, *ibid.*, 4355 (1963). [m] Data are available only for the potassium salt: H. N. Shrivastava and J. C. Speakman, *ibid.*, 1151 (1961). [n] R. F. Bryan, H. H. Mills, and J. C. Speakman, *ibid.*, 4350 (1963).

In Table I are summarized the acids studied. Although no quantitative comparison is available they show marked differences in the rate of uptake of ammonia; benzoic acid reacted completely in 50 hr, whereas the reaction of 2-naphthoic was incomplete after 100 hr. There appears to be not even a qualitative correlation of rate with such physical properties as melting point and acidity ($K_a$) (see Table I). More striking information comes from observation under the microscope of single crystals placed in a transparent enclosure through which was passed a very slow stream of ammonia gas. Most aromatic carboxylic acids whose crystal structures have been determined are known to pack as one or more translationally distinct stacks of hydrogen-bonded dimers. Two crystal habits have been commonly observed:[2] one, needles elongated on a short crystallographic axis and the second, the one of interest here, plates with the most prominent face normal to the longest crystallographic axis (see Table I). When plates of benzoic acid sitting on (001) were allowed to react with ammonia gas the (101) faces could be observed to become opaque rapidly while (001) remained clear. The opaque region was then seen to spread slowly from the side faces toward the center of the crystal while the top (001) face continued to remain relatively clear. Inspection of the crystallographic packing diagram (Figure 1) in the light of these observations both suggests an explanation for the resistance of the (001) face to attack by ammonia and provides evidence for the nature of the (001) face of benzoic acid crystals. It will be seen that if a submicroscopic observer could travel along the *c* axis of the crystal he would pass alternately through layers (parallel to the *ab* plane) containing only hydrocarbon material and through layers containing only the polar carboxylic dimer units. Cleavage of the crystal along a plane between the stacks of hydrocarbon rings should be facile and it is known that cleavage parallel to (001) is particularly easy. Further, the observed slow growth of crystals in the *c** direction during crystallization (as shown by the fact that (001) is the best developed face) might be anticipated due to the fact that an (001) face terminated with benzene ring residues should have little tendency to continue adding benzoic acid molecules back-to-back in the *c** direction. On the other hand, if the surface in the (001) direction developed with exposed carboxyl groups, they should quickly add another layer of benzoic acid molecules in order to complete hydrogen-bonded dimer formation, whereupon growth would be complete. This picture of the surface both explains and is confirmed by the resistance of the (001) face to attack by ammonia since carboxyl groups are relatively unexposed there.

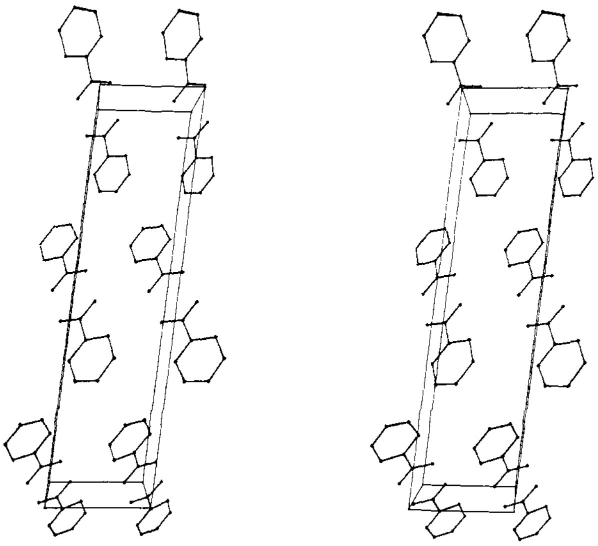

Figure 1. Crystallographic packing diagram for benzoic acid; coordinates taken from reference cited in footnote *a* of Table I. The (001) face of the macroscopic crystal corresponds to the edge of the unit cell at the bottom of the drawing.

This general pattern is followed by the other acids in Table I; in each case there is a habit consisting of plates with the best developed faces nearly normal to the longest axis as was the case with benzoic acid[2] and in each case the best developed face is more resistant to attack by ammonia than are the lateral faces. In each case the packing diagram shows the essential features

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(2) P. Groth, "Chemische Krystallographie," Part IV, W. Engelmann, Leipzig, 1917, p 448 ff.

discussed above although details of symmetry and precise molecular arrangement vary.

Most of the acids listed in Table I have been found to form salts with the composition $(NH_3)\cdot(ArCOOH)_2$ and several of the crystal structures have been determined. Such salts might be expected to be reaction intermediates when the carboxylic acids react with ammonia but we have found no evidence that they accumulate to a detectable extent. Further when platelets of the 1:2 salt of *p*-chlorobenzoic acid were treated with gaseous ammonia they appeared to react as fast as, or faster than, the initial acid (again with strongly anisotropic behavior) to form the 1:1 salt. Principles similar to those discussed for the acids seem to hold for the crystallization and reaction with ammonia of the 1:2 salts.

There remains the question of the mechanism of the incorporation of the ammonia molecules into an already fully packed crystal. A comparison of the volumes per dimer unit of the carboxylic acids with those of the 1:2 ammonium salts calculated from previously available X-ray data shows that there is a volume increase of 6–8% (Table I); earlier density measurements[3] suggest that the addition of two ammonia molecules to form the 1:1 ammonium benzoate produces a total increase of 20–25%. It is not surprising then that disordering accompanies the absorption of ammonia. To investigate this point further X-ray powder photographs of ammonium benzoate and ammonium *p*-chlorobenzoate (the 1:1 salts) were obtained. The same photographs could be obtained by mounting the product from the acid–ammonia reaction without grinding which shows that the product is formed as unoriented microcrystallites of ammonium salt. It seems highly improbable that this reaction is a simple diffusion process: instead ammonia molecules attack a crystal face and formation of ammonium salt loosens successive layers of carboxylic acid molecules in such a way as to permit accelerated diffusion of ammonia into the interior of the crystal.

To determine whether the reaction could be extended to bulkier bases the reaction of crystalline *dl*-mandelic acid[4] with *dl*-2-butylamine, bp 63°, was carried out by placing crystals of the acid in a sealed jar containing a vial of (excess) liquid amine. The vapor pressure was sufficient to permit diffusion of the amine to the acid and a quantitative yield of 1:1 salt was obtained in 96 hr; the salt gave correct microanalytical values without purification. Ammonium *dl*-mandelate, formed by the method employed with the acids in Table I, when submitted to reaction with *dl*-2-butylamine for a length of time which would have caused the free acid to react completely gave no sign of exchange of the amine for ammonia as shown by submitting the product "crystals" to nmr analysis; there was no trace of absorption in the alkyl proton region of the spectrum where the butyl protons should show absorption. Similarly, when the crystalline 2-butylammonium salt of mandelic acid prepared as above was treated with ammonia under conditions which would have caused complete reaction of mandelic acid, microanalysis of the product gave values correct for the unchanged 2-butylammonium salt and showed no indication of any amine–ammonia exchange reaction. It may be concluded that at least in this case the acid–base reactions are irreversible under the conditions employed.

It is hoped that crystal chirality may be utilized to achieve asymmetric induction in the reaction of crystalline acids with gaseous bases.[1b,j,5] Preliminary results have indicated that crystalline (*S*)-(+)-mandelic acid,[6,7] $[\alpha]_D$ 150° (ethanol), in its reaction with an equimolar amount of *dl*-2-butylamine gas shows a preference for the (*S*)-(+) isomer.

It is likely then that reactions between gases and molecular crystals of the sort reported here not only have synthetic value but may also provide valuable insight into the structure of crystal surfaces.

**Acknowledgment.** This research was supported by the Advanced Research Projects Agency of the Department of Defense.

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(3) L. Klemm and W. Klemm, *Z. Phys. Chem., Abt. A*, **151**, 71 (1930).

(4) S. Furberg, *Research* (*London*), **4**, 192 (1951); H. A. Rose, *Anal. Chem.*, **24**, 1680 (1952).

(5) Compare footnote 7 of ref 1h, and F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, **89**, 4099 (1967).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, pp 89, 99.

(7) We are indebted to Professor John Wood, Department of Biochemistry, University of Illinois, for a sample of the optically active acid.

(8) Alfred P. Sloan Foundation Fellow, 1968–1970.

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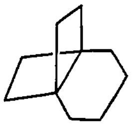
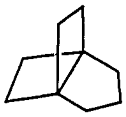
## [4.2.2]- and [3.2.2]Propellanes[1]

*Sir:*

Propellanes are compounds having three rings fused along a common edge.[2] Although a variety of such compounds are known,[3] we report here the first examples containing two fused cyclobutane rings; namely, the [4.2.2]propellane (**1**) and [3.2.2]propellane (**2**) systems. The skeletal requirements of these propellanes are probably best accommodated by near-sp$^2$ hybridization of the quaternary bridgehead atoms; the central bond, then formed to a degree by $\sigma$ overlap of p orbitals, would be expected to be longer and weaker than the usual carbon–carbon bond.[1,3d]



**1**



**2**

Photocycloaddition of ethylene to the enol acetate **3**[4] of cyclohexane-1,3-dione in ether produces the bi-

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(1) (a) Taken in part from the Ph.D. Thesis of Kayson Nyi, The University of Chicago, 1970; (b) a preliminary report of part of this work was presented by one of us (E) at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) The propellane nomenclature for such compounds was introduced by Ginsburg[3a] and apparently has been accepted by the arbiters of such things (see *Chemical Abstracts*). The title compounds, in the Baeyer system, are tricyclo[4.2.2.0]decane and tricyclo[3.2.2.0]nonane, respectively.

(3) For example, (a) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron, Suppl.*, **8** (1), 279 (1966); (b) D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1968), and references therein: (c) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, **88**, 1330 (1966); (d) K. B. Wiberg, E. C. Lupton, Jr., and G. J. Burgmaier, *ibid.*, **91**, 3372 (1969); (e) K. B. Wiberg and G. J. Burgmaier, *Tetrahedron Lett.*, 317 (1969); P. G. Gassman, A. Topp, and J. W. Keller, *ibid.*, 1093 (1969); (f) W. T. Borden, I. L. Reich, L. A. Sharpe, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 3808 (1970).

(4) This derivative of 2-cyclohexenone and relatives bearing an oxygen atom bound to the $\beta$ carbon of the chromophore undergo photocycloaddition reactions very much more sluggishly than cyclohexenones bear-