where, P_{HDO} was obtained as described. As given in Table 3, the value for α gradually increases from 1.128 at 0°C to 1.210 at −38°C. This is substantially different from the calculation made by Miyake and Matsuo (*6*) based on previous data (*3*).

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References

1. Mercury thallium (8.5 percent) in glass (0° to −50°C) calibrated against a platinum resistance by National Research Laboratory of Meterology, Japan.
2. International Critical Tables, vol. III, p. 210.
3. A. Johannin-Gilles and P. Johannin, *Compt. Rend.* **239**, 1470 (1954).
4. I. Kiss and L. Matus, *Magy. Tud. Akad. Kozp. Fiz. Kut. Int. Kozlemeny* **10**, 61 (1962).
5. M. H. Wahl and H. C. Urey, *J. Chem. Phys.* **3**, 411 (1935); L. Merlivat, R. Botter, G. Nief, *ibid.* **60**, 56 (1963).
6. Y. Miyake and S. Matsuo, *Papers Meteorol. Geophys. Tokyo* **13**, 245 (1962).

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Thermal Reduction of Bicarbonate to Formate

Abstract. *Thermal decomposition of infrared pellets of sodium or potassium bicarbonates dispersed in KCl, KBr, or KI matrices leads to the production of bicarbonate monomer ions and finally formate ions, as well as other expected products. These products can be identified readily from the infrared spectra of the pressed disks.*

In 1950 Garrison *et al.* (*1*) irradiated aqueous solutions of CO_2 with α-particles in a cyclotron and showed that the resulting solutions contained appreciable concentrations of formaldehyde and formic acid. These workers suggested that such ionizing radiation might have been one source of reduced carbon compounds in the primeval organic milieu. We wish to report that thermal degradation, under a relatively mild condition, of inorganic bicarbonates dispersed in ionic matrices also produces an appreciable amount of formate.

Our experimental technique was a simple one and was described earlier (*2*). Potassium or sodium bicarbonates were dispersed in optical grade KCl, KBr, or KI powder by the standard method of grinding or freeze-drying. The powder was transferred to an infrared pellet die, evacuated, and then pressed. The resulting disks were heated in an oven in air at constant temperatures ranging from about 450° to 600°C for various lengths of time. Chemical changes in the disks were followed by examining the infrared spectra after the disks had been quenched to room temperature.

Figure 1 shows the changes observed in the spectrum of a typical KBr disk in the characteristic CO-bond stretch region for carbonates. Initially, the spectrum was that of a hydrogen-bonded cyclic dimer of the bicarbonate ion (lower spectrum, *C*), but on heating for a short time the dimers were destroyed. The products in the matrix were the expected carbonate ion (absorption bands *X*, spectrum *B*), some trapped CO_2 gas, and the bicarbonate monomer ion (absorption bands *Y*, spectrum *B*). These products were not due to any contaminants in the disks; other disks prepared in the same manner but without the solute gave none of these absorption bands after they were heated. The identification of the carbonate bands was made by comparing the spectrum to that of a heated disk which contained only potassium carbonate as a solute. The assignments of the bicarbonate monomer absorption bands were made by using the isotopic molecules (deuterium and carbon-13) and by comparing the spectrum to that of the isoelectronic nitric acid molecule. Vibrational frequencies and normal coordinate analysis of the bicarbonate monomer will be reported elsewhere (*3*).

On further heating of the disks, new bands appeared (Fig. 1, absorption band *X*, spectrum *B*), and they were identified as belonging to the formate ion. Spectrum *A* in Fig. 1 is from a heated disk containing potassium formate as a solute. Band *Z* is the antisymmetric stretch mode in the $—CO_2$ group of the formate ion. Other formate bands observed but not shown in Fig. 1 were the CH stretch mode and the angle deformation mode in the $—CO_2$ group. These assignments were confirmed by the use of deuterium and carbon-13 isotopic substitutions. The frequencies of the formate ion in different alkali halide matrices, the changes of the spectra on heating, and the quantitative kinetic study of the thermal decomposition of the formate ion will be reported elsewhere (*4*).

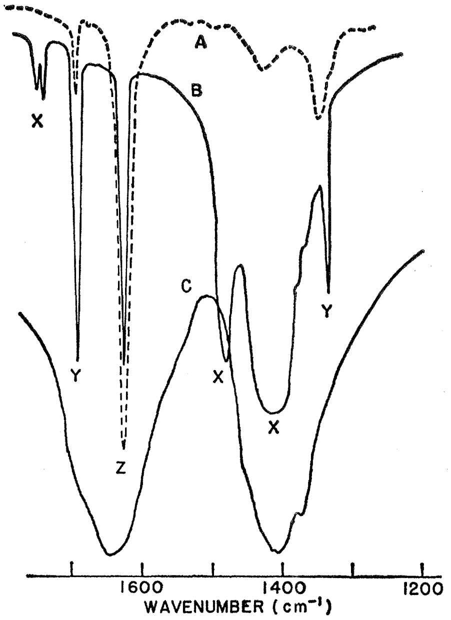

Fig. 1. Infrared spectra of formate and bicarbonate in the region of wave number 1500 cm^{-1}. Spectrum *A*, 0.12 mg formate in 0.5 g KBr heated at 534°C for 5 minutes. Spectrum *B*, 3 mg $KHCO_3$ in 0.5 g KBr heated at 500°C for 200 minutes. Carbonate bands, *X*; bicarbonate monomer bands, *Y*; and formate bands, *Z*. Spectrum *C*, same disk as that used for spectrum *B*, before heating. All spectra were recorded at room temperature. The disks were 1 mm thick by 15 mm diameter.

Figure 2 shows the changes in optical densities of a formate ion band and two bicarbonate monomer bands with heating time in a typical KBr disk. Optimum concentrations for the formation of a bicarbonate monomer was found to be approximately 3 mg of solute dispersed in 0.5 g of matrix salt. The yield of formate ions in such disks was about 5 percent based on initial solute concentrations.

The formate ions resulting from the thermal decomposition of bicarbonate appeared to be well isolated from each other and may have been in solid solution with the matrix salt. Not only were the absorption bands exceedingly sharp, but the ions showed unusual stability toward further decomposition.

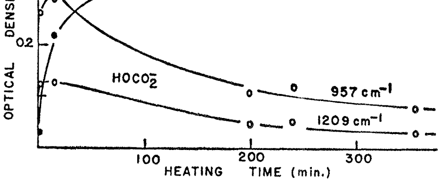

Fig. 2. Changes in the optical density of the absorption bands of formate and bicarbonate monomer with heating time. Data obtained from the sample described for spectrum *B*, Fig. 1. The temperature was 500°C.

Even at temperatures near 600°C, where the KBr matrix itself started to sublime, the optical densities of the formate bands decreased only very slowly. In comparison, the decomposition temperature of pure sodium formate is reported to be about 310°C (*5*). We did not observe formaldehyde in our disks, and this is not surprising since we expected it to decompose readily into H_2 and CO under our experimental conditions. However, formaldehyde is reported to be formed in the pyrolysis of pure sodium formate powder (*5*).

We believe that the reduction mechanism observed in these disks involves the CO_2 anion free radical. This radical has already been identified by electron spin resonance spectroscopy in single crystals of sodium formate irradiated with x-rays (*6*). Evidence for the importance of this radical in our reaction is as follows. First, in KBr, isotopic formates were obtained during the thermal decomposition of oxalates hydrated with H_2O or D_2O. Second, formate appeared as a major product in the decomposition of acetate ion in KBr matrices. Third, we have observed what appears to be the reverse of the free-radical mechanism, namely, the formation of bicarbonate from formate. In thermal degradation studies of potassium formate in KBr matrices (*4*), we invariably observed bicarbonate as one of the minor products (see spectrum *A*, Fig. 1). This bicarbonate was not due solely to hydrolysis of the product carbonate by the atmospheric moisture, since decomposition of deuterium formate gave deuterium bicarbonate. Finally, the electron paramagnetic resonance spectra of our disks showed the presence of long-lived free radicals. The electron spin resonance signals decreased markedly if the disks were ground into fine powders and disappeared completely if the disks were dissolved in water. Details of these studies will be presented later (*4*).

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References and Notes

1. W. M. Garrison, J. G. Hamilton, D. C. Morrison, A. A. Benson, M. Calvin, *Science* **114**, 416 (1951).
2. I. C. Hisatsune and N. H. Suarez, *Inorg. Chem.* **3**, 168 (1964).
3. K. O. Hartman, D. L. Bernitt, I. C. Hisatsune, in preparation.
4. K. O. Hartman, in preparation.
5. R. Toyoda, *Bull. Inst. Chem. Res. Kyoto* **20**, 11 (1950).
6. G. W. Chantry and D. H. Whiffen, *Mol. Phys.* **5**, 189 (1962).
7. Supported by grant NSF-G17346.

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Interaction of Positive and Negative Reinforcing Neural Systems

Abstract. *Evidence is presented indicating that the repetitive turning on and off of reinforcing brain stimulation is not a special property of restricted hypothalamic and tegmental areas. Results from a sample of 22 diverse hypothalamic, septal, amygdala, and hippocampal sites suggest that such behavior can be obtained from most neural areas from which self-stimulation behavior may be elicited. Questions thus arise about the location of aversive neural systems when aversion is considered as being expressed by the act of terminating positively reinforcing brain stimulation.*

Reports that animals will repetitively initiate and terminate electrical stimulation of some brain areas (*1*) has led to speculation that an aversive or negative reinforcing system is activated by prolonged positive stimulation. It has been suggested that this aversive system is activated by a summation of subthreshold stimuli at the periphery of the influenced neural area (*2*). Because these reports have implicated either the hypothalamus or neighboring and functionally allied tegmental areas, interpreters of such data have concluded that aversive and positive neural systems are adjacent to each other in this relatively delimited area (*3*).

We have recently completed a study which suggests that animals will repetitively initiate and terminate reinforcing brain stimulation from most if not all neural areas from which self-stimulation behavior may be elicited. Eighteen rats were implanted with bipolar electrodes of a type previously described (*4*). As four of the animals had two electrodes implanted, a total of 22 neural sites were studied. Histological confirmation of these sites which included diverse hypothalamic, septal, amygdala, and hippocampal (dorsal and ventral) areas is illustrated in Fig. 1 (*5*).

Animals were first trained to press a lever for continuous reinforcement with 0.5-second trains of biphasic rectangular pulses (duration, 0.2 msec; frequency, 100 pulse-pairs per second). After this initial training animals were placed in a plexiglas testing chamber with two levers 10 cm apart, mounted on the front wall. Pressing the left (onset) lever initiated the stimulation train, and responses on the right (offset) lever terminated the train. Animals rapidly learned to turn the stimulation on and off, but in three instances the experimenter facilitated learning by turning off the stimulation when the animal approached the offset lever. This "two-lever" method of determining an animal's preferred duration of stimulation was favored over the "single-lever" method which requires that the lever be held down to receive stimulation. A comparative study of the two methods indicated that animals often terminated the stimulus with the "single-lever" method simply because motoric side effects or the general excitement resulting from the electrical stimulus made them unable to hold the lever down (*7*).

The animals were given five practice tests in the two-lever situation at each of three stimulus intensities. During each 15-minute test only one intensity was presented. Different intensities were presented in a random sequence with an interval of at least 1 hour between tests. A 1-minute "warm-up" period during which time no data were collected preceded each 15-minute test. The intensities selected were derived from preliminary tests: the low intensity was judged to be slightly above reinforcement threshold; the intermediate intensity yielded maximum response rates; the high intensity, which was approximately 75 percent higher than the intermediate figure, resulted in great excitement and in some cases marked motoric side effects.

After the practice tests the animals were given an additional five tests at each of the three stimulus intensities, with all conditions as described for the practice tests. Two of the animals were tested at four intensities. The number of stimulus trains was recorded, along with the total time that the stimulus was left on (duration