each line borrows intensity from all the other multiplet lines, the mixing effect between adjacent lines being dominant. It is possible to allow for different rate constants of relaxation transitions involving different nuclei, but the general result is the same. An important special case is the inclusion of relaxation transitions induced by intramolecular nuclear dipole–dipole coupling. Since this interaction is strongly dependent on the distance between two protons ($\propto 1/r^3$), we may consider only the effects of dipolar coupling within the methyl group.[6] Such a coupling increases the mixing effects of the X quartet line intensities and especially reinforces the borrowing of intensity from second next nearest neighbor lines. As shown in Figure 2b, inclusion of intermolecular spin lattice relaxation cuts the intensity of line 1 to about one quarter of its original intensity. Additional inclusion of dipolar coupling within the methyl group cancels line 1 completely (Figure 2c).

It has long been recognized that the *absolute* intensities of CIDNP spectra are directly proportional to the nuclear relaxation times.[7] Detailed consideration of eq 2 leads to the interesting prediction that the *relative* intensities of multiplet lines in CIDNP should change during the course of the reaction. At the beginning of the reaction, the line intensities are dominated by the first term in eq 2 because relaxation is less important at reaction times short compared to the nuclear relaxation times. This presteady state has a counterpart in the poststeady-state period, after the reaction has been stopped, where the intensities are governed by the relaxation terms in eq 2. The experimental pre- and poststeady-state spectra are shown in Figure 1 (a and c). As predicted, the presteady-state spectrum approaches the one calculated with neglect of relaxation (Figure 2a), with line 1 in absorption. Accordingly, the poststeady-state spectrum shows the same line in emission. The transient intensity of line 1, obtained by recording line 1 repeatedly for a time interval at the beginning and end of the reaction (Figure 3b), demonstrates the mirror-image relationship between the pre- and poststeady-state behavior and shows a striking similarity to the calculated envelopes of Figure 3a.

To demonstrate further the important role of nuclear spin relaxation in CIDNP, the methine quartet was recorded while one of the quartet lines was simultaneously irradiated with moderate rf power so as to diminish considerably the population difference of that line without significant perturbation of the nuclear spin levels.[8] Effective reduction of the strong emission of line 2 or 3 should then lead to absorption for line 1, as indicated by the calculated stick diagrams (Figure 4). Again, these predictions are nicely supported by the experimental spectra shown in Figure 4.

Acknowledgment. K. M. wishes to thank the Stiftung für Stipendien auf dem Gebiete der Chemie for financial support.

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(8) B. D. Nageswara Rao, *Advan. Magn. Resonance*, 4, 271, 286 (1970).

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Stripping Reactions of Gaseous Ions in the Mass Spectrometer

Sir:

We describe a new reaction in gaseous polyatomic ions, some aspects of its mechanism, and its role in generating a new type of mass spectrum of potential analytical value.

We have previously utilized charge-transfer reactions of the type $m^{2+} + N \rightarrow m^{+} + N^{+}$ (where m^{2+} is any doubly charged ion and N any neutral gas or vapor) to separate singly and doubly charged ions in the mass spectrometer and so to obtain pure doubly charged ion spectra.[1] The reverse reaction, leading to an increase in the number of charges borne by the ion, has apparently only been studied for high energy (>10 keV) atomic ions.[2] We now report that the process $m^{+} + N \rightarrow m^{2+} + N + e^{-}$ occurs with facility when polyatomic singly charged ions of 5–10-keV energy impinge upon a variety of collision gases. Moreover, if the collection of singly charged ions formed from a typical organic compound in the ion source of the mass spectrometer is passed through a field-free collision region (pressure of neutral 10^{-6}–10^{-4} Torr), the resulting doubly charged ions can be separated from singly charged ions by operating the electric sector at half the normal value (E) and then mass analyzed to give a new type of mass spectrum (the $E/2$ mass spectrum). The aniline $E/2$ mass spectrum[3] appears in Figure 1; it is juxtaposed against the normal singly charged ion mass spectrum (electric sector value E, ion accelerating voltage V) and the doubly charged ion mass spectrum obtained by charge exchange (electric sector value $2E$). The three spectra are markedly different and experiments are underway to exploit the analytical possibilities of the new type of spectrum by attempting to distinguish isomers which give identical singly and doubly charged ion mass spectra.

It is important to note that with the electric sector set at $E/2$, ions undergoing the reaction $m^{+} \rightarrow m^{+}/2 + m/2$, either collision induced or unimolecular, will be passed. In the aniline case the unimolecular $m^{+} \rightarrow m^{+}/2 + m/2$ process did not give a detectable signal at low collision gas pressures ($\sim 1 \times 10^{-7}$ Torr). Fortunately the collision-induced component of this fragmentation could easily be distinguished from the charge-stripping process using two observations: (i) the charge-stripping process yields maximum signal if the sector voltage is decreased slightly from exactly $E/2$ or if the accelerating voltage is increased to slightly more than V; (ii) peaks due to the collision-induced fragmentation are much broader than those due to the

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(1) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 455 (1970); (b) J. H. Beynon, A. Mathias, and A. E. Williams, *ibid.*, **5**, 303 (1971); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *J. Amer. Chem. Soc.*, in press; (d) T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, in press.

(2) (a) H. Ewald and W. Seibt, "Recent Developments in Mass Spectrometry," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 39. (b) Other references to stripping reactions appear in E. W. McDaniel, "Collision Phenomena in Ionized Gases," Wiley, New York, N. Y., 1964, Chapter 6.

(3) All experiments employed a Hitachi RMH-2 mass spectrometer, modified as previously described;[4] the aniline spectrum was taken using 70-eV electrons, electron current 1 mA, source temperature 150°, source pressure 6×10^{-6} Torr, 8-kV ion acceleration, air as collision gas at 5×10^{-5} Torr pressure.

(4) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 313 (1969).

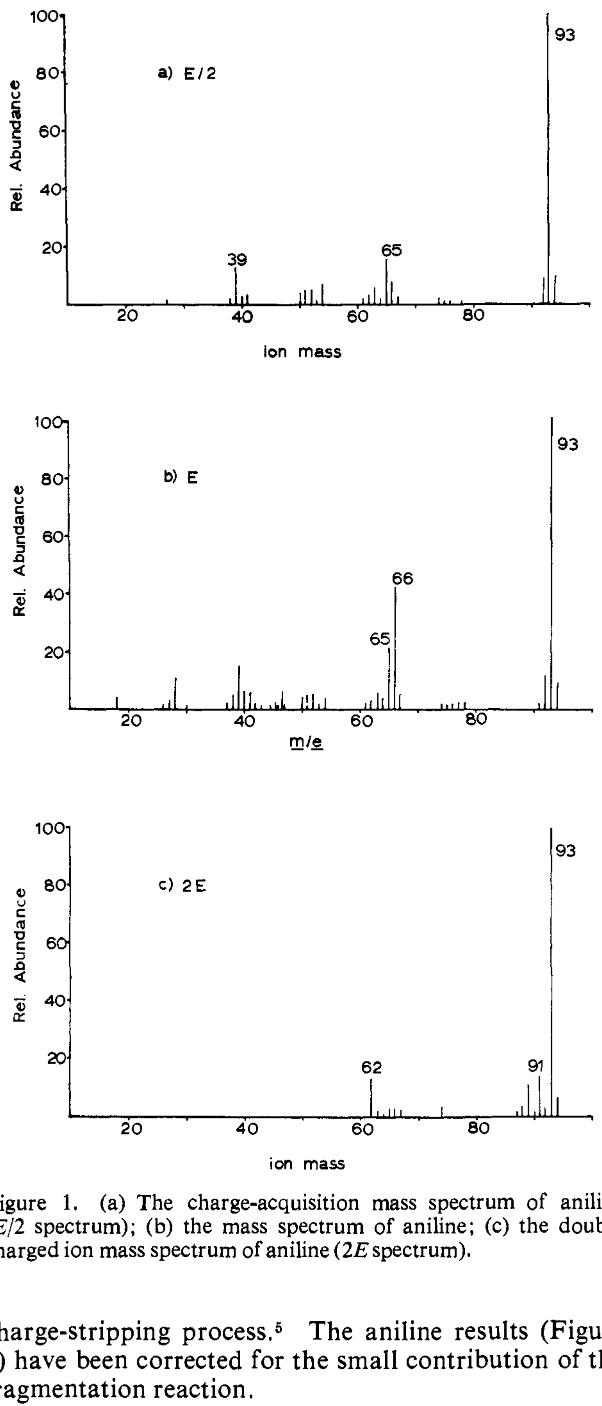

Figure 1. (a) The charge-acquisition mass spectrum of aniline (*E*/2 spectrum); (b) the mass spectrum of aniline; (c) the doubly charged ion mass spectrum of aniline (2*E* spectrum).

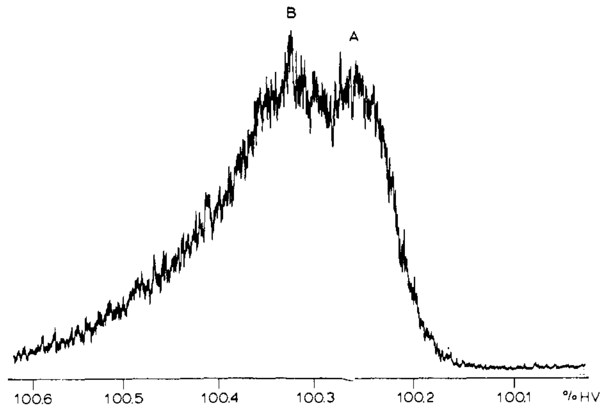

Figure 2. Accelerating voltage scan of *m/e* 15 in NO, with electric sector set to transmit ions which have acquired a charge. B is due to ground state and A to excited NO^+ ions undergoing the transition $NO^+ \rightarrow NO^{2+}$.

charge-stripping process.[5] The aniline results (Figure 1) have been corrected for the small contribution of the fragmentation reaction.

In aniline and benzene the stripping reaction gives, at optimum pressures (*ca.* 5×10^{-5} Torr), a beam intensity about 10^{-3} of that of the main beam of singly charged ions. This is comparable to the intensity (optimum pressures of *ca.* 1×10^{-6} Torr) for the $m^{2+} \rightarrow m^+$ reaction. The differences in optimum pressures point to a stronger collision in the endoergic process and the shift in peak maximum from *E*/2 (or *V*) indicates that the necessary energy is provided from the kinetic energy of the ion. This shift was most conveniently followed by varying the accelerating voltage and it corresponded to a most probable loss of 16 ± 2 eV of kinetic energy in the collision leading to the doubly charged molecular ion in both the benzene and aniline cases. This energy loss was independent of ion accelerating voltage over the range 5–9 kV within the accuracy of the measurement. The differences between the first and second ionization potentials for organic ions are seldom known but in the case of benzene and aniline they certainly are near this value (16.7 eV for benzene-d_1[7]). The range of kinetic energy losses involved in the stripping reaction cannot be estimated from the peak width unless it is assumed that there is no magnification of the kinetic energy of the product ion in the laboratory system.[8] If this assumption is valid the measured width corresponds to a range of energies of ~5 eV at half height for the benzene and aniline molecular ion reactions.

The essentially passive role of the collision gas in the $m^+ \rightarrow m^{2+}$ reaction is brought out by these results for aniline using a number of collision gases (air, oxygen, nitrogen, helium, and benzene): (i) the *E*/2 spectrum is not detectably affected; (ii) the ion yield does not vary widely (certainly less than an order of magnitude with helium and benzene being less efficient than air); (iii) the kinetic energy loss experienced by the ion 93^+ and the range of kinetic energies involved is similar for the different collision gases.[10]

The stripping reaction was also sought in several simpler ions. All rare gases undergo the reaction; so do oxygen and nitrogen molecular ions. Nitric oxide was also examined, and it gives a fairly strong *E*/2 peak which mass analyzes as *m/e* 15 ($30^+ \rightarrow 30^{2+}$).

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(5) Peaks at odd mass which can result only from the stripping process were all sharp; those at even mass were either broad, sharp, or composite (*i.e.*, consisted of both broad and narrow components). Moreover, by scanning the magnet with the sector set at exactly[6] *E*/2 and then repeating the scans at successively lower sector voltages, the sharp peaks increased dramatically in intensity while the intensity of the broad peaks decreased. The shift in the peak maximum for the stripping reaction arises because such reactions will generally be highly endoergic (see later).

(6) The exact center of the broad peaks has not been accurately determined; it is much closer to 0.5000*E* than are the narrow peaks but the possibility that it is slightly offset is not excluded.

(7) F. H. Dorman and J. D. Morrison, *J. Chem. Phys.*, **35**, 575 (1961).

(8) Magnification does occur[9] for fragmentation reactions, where the kinetic energy distribution in the center of mass system is much amplified in the laboratory system. A referee has pointed out that very little if any of this type of magnification will occur for the stripping reaction.

(9) (a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, *A*, **20**, 180 (1965); (b) M. Barber, K. R. Jennings, and R. Rhodes, *ibid.*, *A*, **22**, 15 (1967).

(10) A small dependence of peak shape upon pressure was noted. The corresponding spectra of the rare gases showed greater changes in shape and relative abundance but no gross changes in the positions of the peaks due to the stripping reaction with changes in collision gas. Apparently the collision partner can be excited during the stripping reaction; however, this does not have marked effects upon the *E*/2 spectra studied, hence, the description of the collision gas as passive.

When the magnetic sector was set to pass only ions of m/e 15 and the accelerating voltage was scanned (electric sector voltage being kept constant at $0.5000E$), two peaks were observed (Figure 2).

Peak A corresponds to 30^{2+} ions which have lost 23 ± 2 eV of energy, while peak B corresponds to ions that have lost 29 ± 2 eV. First and second ground-state ionization potentials of NO are 9.25 and 39.8 eV.[11] The difference, 30.6 eV, is in good agreement with the position of peak B. Studies on metastable NO^+ ions[12] have revealed the existence of a highly populated excited NO^+ state 16.9 eV above the neutral molecule. The difference between the energy of this state and the second ionization potential of NO is 22.9 eV, which could very well explain the position of peak A.

It should be emphasized that what we have assayed above is the preliminary analysis of some novel experimental observations.[13] Such possibilities as energy absorption by the collision gas or formation of the doubly charged product in an excited form may, however, be necessary for a complete explanation of the observed peak shapes.

Acknowledgment. Support of the National Science Foundation (GP 16743) is acknowledged.

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(12) T. O. Tiernan and R. E. Marcotte, *J. Chem. Phys.*, 53, 5 (1970).

(13) Seibl[14] has observed the formation of doubly charged ions from superexcited singly charged ions in the absence of a collision gas. This reaction bears some relation to those studied here but kinetic energy loss was apparently not involved.

(14) J. Seibl, *Org. Mass Spectrom.*, 2, 1033 (1969).

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The Preparation and Structure of 2,3,7,8-Tetrachloro-*p*-dioxin and 2,7-Dichloro-*p*-dioxin

Sir:

Current interest in chlorinated dibenzo-*p*-dioxins originated because these compounds are potential impurities in chlorinated phenols and phenol esters, and because 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and hexachlorodibenzo-*p*-dioxin produce severe untoward biological effects.[1] This concern prompted us to establish methods for characterizing some of these compounds. In a conjoining effort,[2] Rowe and others have studied the toxicological properties of the chlorinated dioxins and evaluated in particular the teratogenic[3] and toxic[2,4] effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Available evidence[2] suggests that 2,7,-dichlorodibenzo-*p*-dioxin possesses a low order of toxicity. We describe below the procedures followed in preparing and isolating two chlorinated dibenzo-*p*-dioxins, and their unambigious identification by X-ray diffraction.

2,7-Dichlorodibenzo-*p*-dioxin (DCBD) was prepared by heating a mixture of potassium 2,4-dichlorophenate and a copper catalyst, prepared according to Brewster and Groening,[5] in a stirred slurry with tetralin at 185–210° for 26 hr. The solid product which separated after cooling was collected by filtration and washed with aqueous sodium hydroxide and with alcohol. A single recrystallization from anisole produced the DCBD with an assay of 99.3% as determined by mass spectroscopy.

2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCBD)[6] can be prepared by treating either dibenzo-*p*-dioxin[7] or DCBD in hot chloroform solution with chlorine for periods of 16–20 hr in the presence of catalytic amounts of ferric chloride and iodine.[8] We found that this procedure gave a mixture of chlorinated dibenzo-*p*-dioxins which was predominantly the tetrasubstituted product. Separation of TCBD from the tri- and pentachloro isomers was difficult. Repeated extractions with boiling chloroform, alternated with recrystallizations from anisole, gave after fractional sublimation TCBD which assayed 98% by mass spectroscopy and 98.5% by vapor phase chromatography. The observed melting point was 305° and the heat of fusion was measured to be 9300 cal/mol. Differential scanning calorimetry showed a single exotherm.

The two crystal structures were determined by very similar techniques, and their essential parameters as obtained in our experiments are summarized in Table I. A Picker four-circle automatic diffractometer was used to determine the lattice constants and to gather intensity data in the θ–2θ scan mode using monochromatic Mo Kα radiation. The structures were solved from the Patterson function and refined by full-matrix least-squares assuming anisotropic temperature factors for Cl, O, and C and isotropic temperature factors for H. The assignment of the centric space group $P\bar{1}$ was initially based on intensity statistics and subsequently supported by the anomalous behavior of the metric and thermal parameters upon refinement in $P1$. Corrections were applied for absorption and for anomalous scattering by Cl, and, in the case of TCBD, a secondary extinction correction was also made.

The TCBD crystal contains two independent molecules, A and B, situated on the inversion centers at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), respectively; in DCBD the unique molecule lies on the center at (0, 0, 0). All three molecules approach planarity very closely: no non-hydrogen atom is more than 0.02 Å from the least-

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(1) (a) *Chem. Eng. News*, **48**, 60 (April 27, 1970); (b) E. Hegyi, Z. St'ota, and A. Luptakova, *Berufsdermatosen*, **6**, 327 (1969); (c) G. R. Higginbotham, A. Huang, D. Firestone, J. Verett, J. Ress, and A. D. Campbell, *Nature*, 220, 702 (1968); (d) E. L. Jones and H. Krizek, *J. Invest. Dermatol.*, **39**, 511 (1962); (e) K. H. Schulz, *Arbeitsmedizin-Socialmedizin-Arbeitshygiene*, **3**, 25 (1968).

(2) V. K. Rowe, J. M. Norris, B. A. Schwetz, G. L. Sparschu, P. J. Gehring, J. L. Emerson, and C. G. Gerbig, presented at the 160th National Meeting of the American Chemical Society, Washington, D. C., Sept 17, 1971.

(3) G. L. Sparschu, F. L. Dunn, and V. K. Rowe, *Food Cosmet. Toxicol.*, in press.

(4) W. N. Piper and J. P. Rose, presented at the 160th National Meeting of the American Chemical Society, Washington, D. C., Sept 17, 1971.

(5) R. Q. Brewster and T. Groening, "Organic Synthesis," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 445.

(6) *Warning:* 2,3,7,8-tetrachlorodibenzo-*p*-dioxin is extremely toxic. Techniques used in handling radioactive and infectious materials are applicable to TCBD and include the use of lab coats, throw-away plastic gloves, safety glasses, a laboratory hood adequate for radioactive work, isolated work areas properly identified, minimization of contaminated waste, and safe waste handling and disposal. Hands and forearms should be thoroughly washed after each manipulation.

(7) M. Tomita, S. Ueda, and M. Narisada, *Yakugaku Zasshi*, **79**, 186 (1959).

(8) W. Sandermann, H. Stockman, and R. Casten, *Chem. Ber.*, **90**, 690 (1957).