Explosive Molecular Ionic Crystals

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In ionic crystals of the form M^+X^-, certain covalently bonded anion groups X^- are particularly associated with instability. The heavier metal cations M^+ enhance this. Very sensitive explosives occur within the extended azide family, where $X^- = CNO^-, N_3^-, NCO^-$, or NCS^- (an isoelectronic set of unsaturated linear triatomic anions). Another such family are the globular oxyanions $X^- = ClO_2^-, ClO_3^-, ClO_4^-, NO_3^-$, and MnO_4^-. Mishandling of NH_4NO_3 or NH_4ClO_4 has caused major disasters. An irreversible cyclic mechanism is proposed for such decomposition, involving mechanoelectronic band-gap excitation and coalescence of X with X^-. From an intracrystalline ion-molecule collision complex, the singly charged dianion X_2^-, exothermic reactions proceed with high yield.

FOR MOST CRYSTALLINE MATERIALS, THE RESPONSES TO moderate mechanical stress amount only to mechanical failure of the lattice. However, mild working may detonate CuN_3. This is a dramatic but little understood process of chemical decomposition, propagating somewhat faster than sound. It is still disputed whether detonation can be described in terms of equilibrium (as thermal, quasistatic, or reversible), either for the primary (*1, 2*) or for the secondary (*3*) explosives. The primary or initiating explosives typically are molecular ionic crystals. The secondaries are less sensitive materials, used for bulk energy storages; these are molecular or van der Waals crystals (*4*).

This article addresses only the former group. An irreversible decomposition loop is proposed, initiating with mechanoelectronic band-gap excitation. Upon pulsed optical band-gap excitation of NaCl (a much easier study), the initial nuclear motions are not thermal; in fact they are quite indifferent to the lattice temperature (*5*). The large exothermicities of the azides can support very energetic unit processes, even in thermal decomposition (*6*).

The initial focus is on the monovalent metal azide crystals, which suggests the acronym MMA. The lattices (7) are simple—tetragonal distortions from the CsCl type (Fig. 1), except that for NaN_3 and LiN_3 they are distortions from the NaCl type (Fig. 2). We extend our prototypical class MMA to include the other anions of the azide family: fulminate, CNO^-; isocyanate, NCO^-; and isothiocyanate, NCS^-. Explosives included among these then are the CsCl-type azides of Rb, Tl, Ag, and Cu (extremely sensitive) (*8*), and the fulminates of both types (*9*).

At the outset the model hinges upon the similarity (assumed with some justification) of the MMAs to the corresponding alkali halides, in regard to crucial lattice relaxations following electronic excitation. Subsequently an argument is developed that the mechanistic essentials may extend to other lattices and anion groups. Molecular anions are sometimes termed "pseudohalides"; an example is N_3^-, which resembles Br^-. Though shaped as a compact prolate spheroid, it has similar volume and similar electron affinity (*10*). These likenesses are significant in regard to lattice relaxations.

In alkali halides, Linke and co-workers demonstrated mechanoluminescence in the exciton bands, and other evidence of mechanically induced excited states (*11*). In much earlier studies of NaCl, KCl, and CsI, Belyaev and Martyshev (*12*) found that fracture of crystals gives rise to various electrical phenomena, including optical and radio emission. Characteristic emission was observed for fracture under air (N_2 bands) or argon. Molotskii (*13*) argued that the decomposition of alkali halide crystals during fracture is distinctly mechanolytic, the temperature rise and the thermal rates being small. No specific mechanisms have been established for such effects.

One account is as follows: Moving dislocations actively sweep charged defects to surfaces. At separating surfaces, facing patches of opposite sign are formed (*11*). This sets up an electric field independent of separation until the distance approaches the patch diameter. Mechanical work against the field then may generate large potential differences (*13*). Charged particles escape surfaces and enter oppositely charged surfaces, creating radiation damage and more charges; this accelerates as the crystal is worked. One energetic electron will give rise to many excitons (*14, 15*), each leading to the excitonic chemistry discussed below.

Proposed Mechanism

For soft crystalline solids, Coffey has described evidence that localized energy concentration is chiefly due to shear-band formation (*16*). Let us suppose that such mechanical working has somehow given rise to be a population of excitons (*11, 17*). By virtue of a lattice instability detailed below, the neutral N_3 (or CNO, or other X) playing the role of hole is propelled directly into impact with a neighboring N_3^- (or other X^-). In this "ion-molecule" collision, the $(N_3)_2^-$ complex fragments with high yield. This disrupts the lattice further (*18*) and mechanically produces more excitons, to reenter the cycle.

Nuclear Relaxation and Relocation in Excitonic States

In alkali halide crystals, and evidently in related salts, the vertical excitonic states (all nuclei taken as fixed) are not mechanically stable; the lattice undergoes relaxation. On the ground excitonic surface, remarkably extensive relocation of halogen nuclei occurs, through linear replacement sequences (see Fig. 2) and through angular reorientation of certain axial centers (*5, 19, 20*). For the NaCl-type

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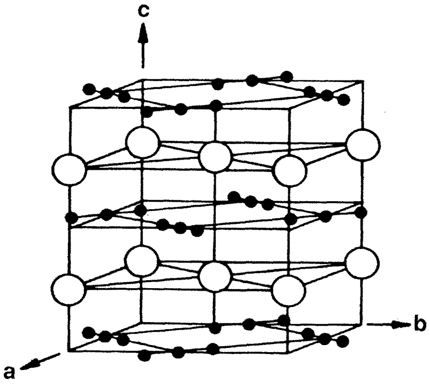

Fig. 1. Tetragonal structure, modified CsCl-type of KN_3-type azides. Axes *a* and *b* are equivalent. The N_3^- groups are less elongated than is suggested; their electron clouds, shaped as compact prolate spheroids, are only 44% greater in length than in width (*10*). Reproduced from (*7*), with permission.

alkali halides, extensive studies have been performed of a variety of processes of this nature: (i) coloration—Frenkel defect-pairs, F and H centers (*21*) are formed; (ii) the inverse process—a migrating H center, recombining with an F center, gives rise to exciton luminescence (*22*); (iii) surface ejection—atoms are expelled from the crystal (*23*); and (iv) macroscopic length changes—as H centers are optically reoriented (*24*). The CsCl-type alkali halides have been studied less exhaustively, but it is clear that similar transport of atoms occurs in them. They differ in that the axis of linear transport is ⟨110⟩ for NaCl-type but ⟨100⟩ for CsCl-type (*21*). Radiative coloration of CsCl-type alkali halides is well known, and optical bands of the F and H centers have been assigned (*25*). Kravchenko *et al.* (*26*) studied CsBr with pulsed excitation techniques comparable to those used by Williams *et al.* for NaCl-type materials (*5*). Obtaining corresponding time-dependent spectra, they gave a similar interpretation in terms of halogen transport processes.

A detailed theory has been given for lattice relaxations and nuclear transport in NaCl-type alkali halides (*19, 20*). Two incremental coordinates are introduced, Q_1 and Q_2. Grossly, they represent motions along the transport axis, of two halogen nuclei regarded instantaneously as the principal players—initially the neutral X resulting from vertical electronic excitation, and a neighboring X^-. There are concomitant displacements of many additional nuclei (*19, 20*); the minor players define the strain field (Fig. 2). Under Q_1, the two nuclei move toward their mutual center to form covalently bound X_2^-, similar to the species Cl_2^-, which is stable in free space (*27*). Q_1 has even symmetry with respect to the mutual center of X and X^- (not with respect to any lattice site). For the higher excitonic states and for continuum states, this completes the relaxation; X_2^- takes the character of an isolated hole, a V_k center (*28*).

In the ground-state exciton, the excited electron is maximally localized (subject to orthogonality to the crystal ground state); it competes for phase space. According to the "off-center" model developed for the NaCl type (*19, 20*), Q_1 relaxation alone does not achieve stability. As Q_2 varies, the nuclei comprising X_2^- are displaced as a unit, along the transport axis (*29*). The first ground-state minimum with respect to Q_2 occurs at a configuration of neighboring F and H centers, defining the self-trapped exciton (*20*) or STE (see Fig. 2). Further minima, for increasingly separated F and H centers, are also accessible on the ground-state surface in steps of a ⟨110⟩ replacement sequence over modest barriers (~0.1 eV). The F, H, and STE are identified in Fig. 2. It can be seen that the initial motion of Cl^- is retrograde, toward the advancing Cl (Fig. 2b). Here the sequence has a length of two unit cells. The probability distribution of such lengths is not well known. Subsequently, thermal agitation may cause the split-interstitial pair, or H, to migrate further or to reorient to another ⟨110⟩ axis.

Electron spin resonance (ESR) and optical studies indicate that the CsCl-type alkali halides support very similar Q_1 relaxation, again forming X_2^- molecular units. And again, as for the NaCl type, they indicate thermally activated Q_2-like axial transport, and reorientation (*30*). The axis of a V_k or of an H center, like the transport axis, is ⟨110⟩ for the NaCl case (Fig. 2) but ⟨110⟩ for the CsCl case (Fig. 1). In a V_k center, X and X^- are separated by two and by four closest M^+ ions in the respective cases. In an H center, X shares a site with X^- for either case (*21*). Passage of X through the cation frame imposes the potential barriers mentioned above. Song *et al.* (*19, 20*), presenting a detailed quantum chemical model for formation of the STE in the NaCl-type alkali halides, stated that the driving force for Q_2 relaxation arises from the attraction of the excited electron for the developing vacancy and its repulsion of the Cl_2^- ion. Extension of the theory to the CsCl type should again support an off-center STE. Finally, the experiment of Kravchenko *et al.* (*26*) affords a clear demonstration of ⟨100⟩ replacement sequences.

In the MMAs, excitation above the band gap or into excitons attached to it (*14, 15*) should give rise to similar transport. Several azide crystals exhibit distinct coloring: NaN_3 and KN_3 (NaCl type), RbN_3 and CsN_3 (CsCl type). This has indeed been attributed to F centers (*31*). No clear picture has been given of the H center (*21*). Consider the relaxations to be expected in NaCl- and CsCl-type MMAs, when excitation replaces X^- by neutral X (subsequently, for an interacting pair X, X^-, I will refer to the excited electron and to the "remaining" electron). Forces similar to those in the alkali halides should again lead to X_2^-, first in a V_k then in an H configuration, unless cluster-ion fragmentation intervenes or a high barrier is encountered. The coordinate Q_1 is clearly important, leading to the intial X_2^- complex. Q_2 may seem less essential, but this is arguable.

Chemistry Within the Dianion

In principle at least, real-time observations might determine whether replacement sequences actually occur, and whether X_2^- fragmenting reactions proceed from V_k or from H configurations. Absent such data, there is a pattern of behavior versus anion shape that may reflect the facility for Q_2-type motion and thus the importance of such transport: The azide family of anions, which includes mechanically sensitive explosives, are linear triatomics. In the abstract, they are ordered by decreasing sensitivity. Evans and Yoffe (*32*), whose ideas somewhat anticipated the present paper, believed that the greater stability for NCS^- might be due to the excess size of the sulfur atom. The globular oxyanions are less commonly known for extreme mechanical instability, but many salts are thermally unstable. Salts of the larger chlorine oxyanions are progressively more stable. These considerations suggest that the essential reactions require the H-center configuration, with both nuclei of X_2^- in a common cell and sharing one potential minimum. The primary yield of F centers is clearly high for the alkali halides (*15, 20, 26*), and H arises jointly with F. A large yield is likely for the MMAs as well.

Do X and X^- simply coalesce in the MMAs, as do Cl and Cl^- in NaCl? For Cl_2^- in the V_k configuration, though the two nuclei still lie in neighboring cells, the remaining electron is already shared between them (*19*). Relaxation along Q_1 here has lowered the energy; the $^2\Sigma_u^+$ ground state potential curve for Cl_2^- (in free space) is attractive for all separations greater than R_e = 2.65 Å, binding the nuclei by 1.28 eV (*27*). Such data are not available for N_3, N_3^-, and putative $(N_3)_2^-$. Still, each of the two N_3's is attractive to the remaining electron (*10*), and one might suppose that they will minimize the energy by sharing it as in Cl_2^-. Dimerization from unsaturated molecular ions reacting with their neutral parents is well precedented, as for neutral allenes (*33*). The entity $(N_3)_2^-$, however, is probably unstable (*6*).

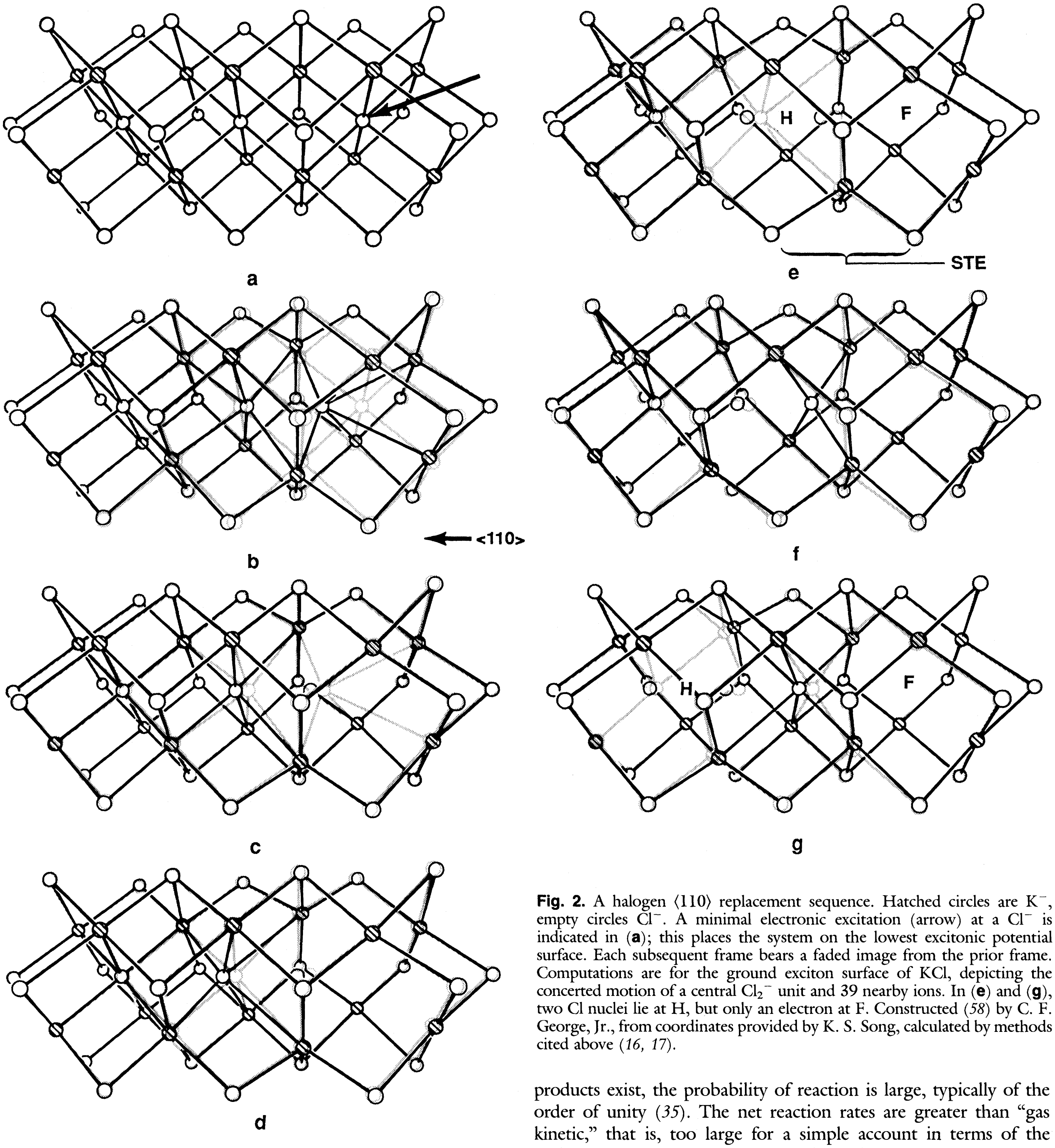

Fig. 2. A halogen ⟨110⟩ replacement sequence. Hatched circles are K^-, empty circles Cl^-. A minimal electronic excitation (arrow) at a Cl^- is indicated in (**a**); this places the system on the lowest excitonic potential surface. Each subsequent frame bears a faded image from the prior frame. Computations are for the ground exciton surface of KCl, depicting the concerted motion of a central Cl_2^- unit and 39 nearby ions. In (**e**) and (**g**), two Cl nuclei lie at H, but only an electron at F. Constructed (*58*) by C. F. George, Jr., from coordinates provided by K. S. Song, calculated by methods cited above (*16, 17*).

A useful perspective is afforded by the "ion-molecule" literature (*34, 35*), which treats reactive collision rates for molecular ions and molecular neutrals (here X^- and X) in the gas phase. Two peculiar features are recognized, both arising from attractive polarization forces (*36*): (i) There is a large cross section (>100 Å^2) for commitment to collision, considerably exceeding the physical size of the objects (*34*). The importance of this seems diminished in the intracrystalline context, because X is channeled directly toward X^-. (ii) The more essential point concerns the "intimate" collision developing as the separation of X and X^- decreases, beyond the initial commitment. Where exothermic or thermoneutral candidate products exist, the probability of reaction is large, typically of the order of unity (*35*). The net reaction rates are greater than "gas kinetic," that is, too large for a simple account in terms of the molecular sizes. $X + X^-$ reactions from the H configuration may reasonably be favored by linear X, and by-products such as N_2 and CO; these are very exothermic and close-knit molecular units.

Talrose *et al.* (*35*) presented reasons for the high reaction efficiency of these intimate collisions, including the following two: The first concerns the reaction barrier, well known for neutral-neutral encounters. (Even if the channel is ultimately exothermic, the bonding orbitals must reorganize, abandoning the binding energy of the initial groups before recovering the corresponding energy in the products.) Neutral-neutral rates, in fact, are typically much slower than gas kinetic, $<1\%$ (*37*). While similar barrier effects must be present in ion-molecule encounters, the attractive polarization force assists passage. Second, the mutual attraction of the partners may give rise to a long-lived complex, enhancing the net probability of reaction.

In collision, X and X^- need not emulate Cl and Cl^- by integrating as a single molecular ion. There may be highly exothermic exit channels, and X_2^- may not exist as a stable entity. This is presumably the case for $N_3 + N_3^- \rightarrow (N_3)_2^-$, where $3N_2$ is the obvious exothermic product, apart from charge (*6*). From simple azides under band-gap excitation, a variety of ESR signals have been interpreted as decomposition products of such reactions (*38*). The more confident assigments include neutral N [from NaN_3, KN_3, RbN_3, CsN_3 and $Ba(N_3)_2$], N_2^- (from NaN_3 and KN_3), and N_4^- (from KN_3 and RbN_3). This is to be compared with (*39*), where also a number of competing exit channels were found.

The pairwise character of the reactions through X_2^- suggests ways to test the model, parallel to the gas-phase studies (*39*), with isotopically labeled or mixed materials (for example, N_3 + CNO). In this vein, Boddington and Iqbal (*40*) believed that explosive decomposition of the fulminates (X^- = CNO^-) proceeds through two CNO units, yielding simply $2CO + N_2$. Slow thermal decomposition, in contrast, gives complex, even polymeric, products.

An Efficient Closed Loop of Decomposition

To recapitulate, the sequence of events begins with a population of excitons produced by mechanoelectronic effects in worked material: (i) Each one incorporates or gives rise to one dianion X_2^-, through lattice relaxation. (ii) Fragmentation occurs from these X_2^- complexes, likely again with high efficiency. There is ambiguity between the V_k and H forms of X_2^-, but the H configuration is preferred. (iii) X_2^- fragmentation and interstitial gas products disturb the lattice, locally or in macroscopic strain fields. Annealing may compete and so contribute to definition of a threshold. These processes cannot be detailed, nor can their efficiencies be estimated. (iv) Disruption of the lattice creates more excitons mechanoelectronically, closing the loop. These effects are even more difficult than the prior group, in regard to engineering characterization.

Fragmentation of $(N_3)_2^-$ probably does not yield much more than 10 eV (*6*). Each such event must give rise to another exciton, of energy ~6.5 eV (*6*), if the cycle is to be perpetuated. It seems that any rational model cycle must exhibit two opposing features: First there must be a barrier, since the crystals are metastable. There is evidence favoring band-gap or exciton energy for that role. Second, the ~10 eV released on each passage must be marshaled with adequate efficiency for yet another passage over the barrier. If not (iii) and (iv), other efficient mechanisms must be postulated to close the hypothesized cycle.

The literature contains ample evidence of intertwining mechanical, electronic, and chemical processes: (i) Begg *et al.* (*41*) demonstrated a striking mechanolytic effect in $NaClO_3$: Heating, even far below the temperature required for simple thermal molecular dissociation, causes a limited but significant level of decomposition. This is mediated through strain centers; it is enhanced by borax impurity, which tends to alter the lattice structure. (ii) Studying AgN_3, Tang and Chaudri (*42*) found that dielectric breakdown and subsequent explosion were produced by dc electric fields as low as 130 V/cm, with time delays up to several days. They associated this with carrier injection and drift of Ag^+ ions. Such delays clearly do not represent accumulation of thermal energy, but more probably of defects. (iii) Under some conditions, PbN_3 crystals growing from aqueous solution may explode spontaneously (*2*). (iv) See again Audubert's description of ultraviolet luminescence attending thermal decomposition of azides (*6*).

Thermal Decomposition, the Traditional Hypothesis

This alternative picture has its own limitations, particularly if taken in simplest form: spatially progressive decomposition through forward transfer of energy by thermal diffusion alone. This may describe deflagration, a relatively mild mode resembling burning. A detonation front, however, advances at ~5 km/s. Speed of this order strongly implies that mechanical effects are limiting and hence essential. A shock front could be responsible for the spatial advance of energy, but dissipate to heat before initiating further decomposition thermally. This is akin to the nonthermal model proposed above but is minimally efficient by definition; the energy is distributed over all degrees of freedom. Here it is hypothesized that there exists a more specifically directed channel for expression of an advancing front of mechanical energy, to reenter the cycle; if so, it will dominate.

Other Materials; the Generality of Dianion Formation

Seeking to exploit a kinetic analogy to alkali halides, in which Q_1 and Q_2 transport have been demonstrated, I have thus far focused on the MMAs; there the analogy is closest. I have noted above that these anions usually induce only rather simple modifications of the NaCl- or CsCl-type salt lattice. In considering extension of the model beyond the MMAs, we must recognize that the characteristic lattice relaxations depend upon valence, coordination number, lattice structure, and bonding type (heteropolar versus homopolar between M and X).

In a number of sensitive crystals, the metal ions are divalent or of still higher valency. Many of these are significantly homopolar. Diverse coordination structures and lattice types, polymorphism, and thermal phase changes reflect interplay between directed and nondirected bonding (*7, 9*). Relaxations like Q_1 and Q_2 are also known for the divalent fluorite structure. Song *et al.*, in a theoretical treatment similar to that cited above for the NaCl-type alkali halides, again found dianion formation [in addition to linear transport, there is also a rotation (*43*)]. Such relaxations likely will again lead to chemical instability. It is reasonable that the model may be extended to still further classes, appealing in general to the reduction of energy as X and X^- coalesce to X_2^-, allowing the remaining electron to be shared between the two electronegative groups.

The globular oxyanions comprise a second major family associated with instabilities (*44*). The metal chlorites decompose between 100° and 200°C, the heavier ones explosively; NH_4ClO_2 decomposes within hours at 25°C. The metal halates, perchlorates, and permanganates are generally more stable, but $AgClO_4$ is considered a sensitive explosive (*4*). The ammonium halates and permanganate are quite unstable. NH_4ClO_3 and NH_4BrO_3 decompose slowly at 25°C. They and NH_4MnO_4 explode between 50° and 100°C.

The NH_4^- cation introduces exothermicity, complex chemistry, and temperature-dependent competition among channels (*44, 45*). Several decomposition mechanisms have been proposed. One initiates with proton transfer to the anion (*44*). Less obviously, NH_4^- may contribute temperature-dependent instability through physical effects of thermal agitation by the hydrogens. Thus the efficiency of transport to a critical "H-center" configuration might increase rapidly with temperature, leading to X_2^- processes. Related effects are known; for example, the thermal expansion coefficients of NH_4Cl and of NH_4Br are anomalously large and temperature-dependent (*46*).

NH_4NO_3 and NH_4ClO_4 are much less delicate than the halates, but still capable of detonation (*47*); each has powered major industrial disasters (Fig. 3) (*48*). In preparation for use in fertilizing or explosive mixtures (NH_4NO_3) and in rocket propellant (NH_4ClO_4), they are gathered in great bulk. Imperfect isolation from flammable materials is likely; asphalt (*49*), oil, and vehicle tires, for example, may be enlisted as fuel. The importance of excluding halate and permanganate impurities has also been recognized (*45, 47*). It has been inferred that the explosive sensitivity of these "oxidants" may depend significantly upon the temperature (*49*), consonant with the discussion above. Evidently a localized, essentially fuel-limited fire can promote a large mass successively to deflagration and detonation.

Other explosive ionic crystals are still more complex, and further removed from prototypical MMAs. Yet their decomposition may again involve band-gap excitation, mediating coalescence of anion material. Some diacids form unstable salts with double-ended divalent anions; examples are oxalate and malonate (*1*), and acetylide may be appended (*4*). The styphnates belong to a trinitroaromatic diacid, $C_6H(OH)_2(NO_2)_3$, the anion resembling secondary explosive species; not all the metal and oxygen nuclei are coordinated equivalently (*50*).

Homopolarity; the Structure of the Band Gap

Within a series of unstable salts (say the azides), those which are more ionic, more heteropolar between M and X, are progressively more stable (*32*) [even the most ionic fulminates explode, however (*9*)]. Thus it may seem problematic that our model for explosive behavior begins with lattice relaxations typical of ionic crystals. However, even the alkali halides, in which Q_1 and Q_2 were studied, do not attain perfect heteropolar bonding (*51*); the picture oversimplifies halides as well as pseudohalides. Quite generally in formation of an ionic crystal from the elements (or a neutral radical might be substituted), the transfer $M + X \rightarrow M^+ + X^-$ is incomplete, and the consequent orbital is somewhat homopolar. The reverse transfer exists as a low-lying excitation of the crystal; but the requisite energy or band gap is reduced by virtue of the incomplete transfer at the outset.

Evans and Yoffe entertained a similar view (*32*). Finding an anticorrelation of band gap and sensitivity in a series of metallic azides, they asserted that their decomposition must depend upon the formation of neutral azide radicals. In the present model, this occurs as a basic premise. Taking the band gap as a critical excitation energy, the above authors felt that the anticorrelation actually accounted for the variation of sensitivity within the series.

Conclusion

Additional experimental and theoretical tests for reactive X_2^- collision complexes would be very valuable. Optical excitation may circumvent the refractory nature of mechanoelectronic effects in the framing of well-controlled experiments, and enable study of the central microscopic processes in isolation from the macroscopic effects of lattice failure. The anisotropy of the KN_3 lattice, for example, would allow an optical electric field vector to be oriented perpendicular to the azide-ion axes. With a tunable laser, one might distinguish between band-gap and intra-anionic excitations (*17*).

This article has presented a microscopic model for unstable or explosive behavior in many molecular ionic crystalline materials. Though grossly ionic or quasi-ionic in the sense discussed by Phillips (*51*), their anions X^- are covalently bound groups rather than atoms. The central hypotheses are that they emulate alkali halide crystals in regard to the transport of anion material, induced by band-gap excitation; and that coalescence of X and X^- gives rise efficiently to the characteristic decomposition chemistry.

Fig. 3. Texas City, Texas, 16 April 1947 (*55*). The French freighter S.S. *Grandcamp* was at pier in this very busy industrial area. Fire began among bags of NH_4NO_3 totaling 1400 tons. When firefighters seemingly had gained control, the ship was obliterated by an explosion. Flaming bales of hemp were sent flying, propagating fires. The S.S. *High Flyer*, also laden with nitrate, exploded 16 hours later. At an adjacent Monsanto synthetic rubber plant built in World War II, 227 lives were lost. Nearby oil refineries and associated facilities were destroyed. See (*48*) for further history of major catastrophes of a similar nature. [AP/Wide World Photos]

These materials also emulate simple molecular or van der Waals crystals, in that they afford a constraining environment for the anion groups X. Two classes of effects may be contemplated: First, the lattice (Fig. 1) may fix reactive groups in definite steric relations [or it may not; for sufficient temperature, N_3^- can rotate (*7*)]. In these systems, it is not clear whether the reactions actually reflect such "topochemical" factors (*52*). Second, reaction products produce a lattice strain field (*18*). Conversely, work invested in lattice strain (Fig. 2) modifies the effective free energy of intracrystalline reactions (*5*). Molecular ionic crystals define an interesting area of solid-state photochemistry, exhibiting a close relation between phenomena traditionally studied by solid-state physicists and by chemists.

Finally, it demands emphasis that explosion hazards can arise in diverse conceptual contexts. While massive destruction is invited by vast bulks of NH_4NO_3, NH_4ClO_4, and similar salts, the more sensitive materials are dangerous in relatively minute amounts. Some, such as $AgClO_4$, might be generated in deliberate procedures, without knowledge of the hazard (*53*). Some might be generated inadvertently; NaN_3 solution, poured down a drain into lead plumbing, can precipitate relatively insoluble and explosive PbN_3.

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48. Propagating decomposition in molecular ionic crystals has underlain several uncontrolled large-scale explosions:

    1921—Two blasts in German areas, the greater at a BASF plant (*54*) in Ludwigshafen (the suburb Oppau), on the Rhine. An explosion occurred in ~4000 tons of a double salt, NH_4NO_3/NH_4SO_3, probably from blasting to break up caked matrial. Net toll: ~1000 lives (*4*)

    16 April 1947—Texas City, TX, at the pier (Fig. 3). NH_4NO_3 had been mixed with 1% mineral oil and 5% kaolin, probably to prevent caking. Unfortunately this is an easily initiated mix (*4*). Destroyed were two nitrate-laden freighters and a huge Monsanto plant, other ships, barges, refineries, an oil train, and two light aircraft overhead. At a range of 2 miles, two persons in an automobile were killed by flying sheet metal. A 10,640-pound anchor was blown half a mile. Windows were broken in Baytown, 25 miles away. Net toll: 576 lives, 27 firefighters (*55*).

    4 May 1988—Henderson, NV. More than 8 million pounds of NH_4ClO_4, in several blasts over 15 min, destroyed the PEPCON plant. This was one of two national facilities to make the oxidizer for solid rocket propellant. Fire may have been started by molten iron from welding. Material allegedly was in contact with such fuel as asphalt and plastics, and a 16-inch natural gas pipeline lay underground. There was extensive property damage in the city, and some to a radius of 20 miles. Richter readings of 3.0 and 2.5 were recorded in California (*56*).

    29 November 1988—Kansas City, KS. At a construction site, one of two trailers of NH_4NO_3 was set afire. Both exploded, making craters 30 to 40 feet wide and 7 feet deep. Windows in surrounding neighborhoods were broken. Two firetrucks were destroyed, one obliterated. Six firefighters died (*57*).
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