

Decomposition of Solid Barium Nitrate by Fast Electrons

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Effect of Temperature on the Mass Spectra of Hydrocarbons

R. E. FOX AND J. A. HIPPLE

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February 26, 1947

SEVERAL years ago one of us reported a marked temperature effect on the relative peak heights observed in the mass spectra of hydrocarbons.¹ As this work has not previously been published, it would appear desirable to describe the experiment now in view of the recent interest expressed in it privately.

Figure 1 shows the ion source of the mass spectrometer tube used in the investigation. The thermocouple on the gas inlet block (3) should provide a fairly good measure of the temperature of the gas emerging from the small slit in it and crossing the electron beam. The ions formed by electron impact are then accelerated through the slits in electrodes (2) and (1) and pass into the conventional analyzer of the sector-field type. The temperature of (3) was varied by adjustment of a furnace wrapped around the glass envelope of the ion source.

Using a mixture of isobutane and neon, the intensities of various ions in isobutane relative to Ne^{20+} were measured

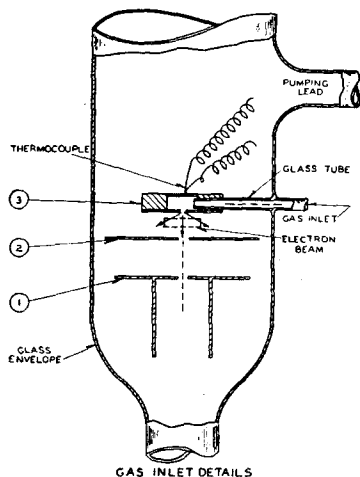


FIG. 1. Arrangement of ion source for studying the effect of temperature on the mass spectra of hydrocarbons.

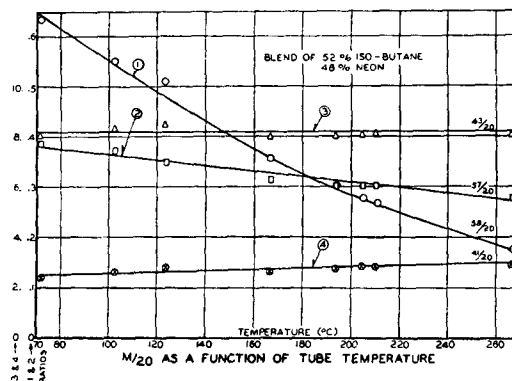


FIG. 2. Variation with temperature of several ions observed in isobutane (neon used as internal standard).

for various values of the temperature of (3). These data are plotted in Fig. 2. It is seen that there is a very marked dependence on temperature of the $\text{C}_4\text{H}_{10}^+$ ion. In fact, this ion is almost twice as abundant at 70°C as the C_4H_9^+ ion, becoming equal to it at approximately 180°C and is relatively less abundant at higher temperatures. Thus, the ratio of these two peaks may be used to measure the temperature of the source. The mass 58 peak in *n*-butane has a similar temperature dependence. Other hydrocarbons show an even greater variation of the spectrum with change of temperature. For instance the parent peak of 2,2,3-trimethylpentane is more than five times as large at 175°C than it is at 225°C . Other peaks in this spectrum show changes that are less pronounced.

¹ J. A. Hipple, reported at the St. Louis meeting of the American Institute of Chemical Engineers, November, 1944.

Decomposition of Solid Barium Nitrate by Fast Electrons*

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February 21, 1947

THE behavior of irradiated salts on solution is an almost unexplored subject, which has become of interest recently in connection with production of radioisotopes.

During 1944, the authors had occasion to irradiate ordinary C.P. grade barium nitrate crystals with a beam of 1.2-Mv electrons from a Van de Graaff generator. On dissolving the irradiated salt in water, copious effervescence occurred, and nitrite was found in the solution.

In one experiment, the salt was irradiated in a small closed glass vessel under helium; the energy dissipated was 1.1 watt-hr./g of salt. After irradiation, the vessel was evacuated and water was admitted; gas was evolved on solution to the extent of 0.9 cc/g of salt. Analysis showed the gas to contain 3 percent of hydrogen; the balance contained no acid gases and was presumed to be oxygen. The solution contained nitrite ion.

In a second experiment, the salt was irradiated while

TABLE I. Formation of gas and nitrite on solution of barium nitrate irradiated with 1.2 Mv electrons at a rate of approximately 1.5 watts/g.

Irrad. time, hr.	% NO ₂ ⁻ converted to NO ₂ ⁻	Gas formed, cc/g (22° C, approx. 73 cm)	Calc. O ₂ equiv. to NO ₂ ⁻ found, cc/g (22° C, 73 cm)
2.8	5.5	5.9	4.9
6.0	10.5	10.1	9.0
9.6	13.0	12.8	11.5
13.0	18.0	16.4	16.0
17.3	21.1	19.0	18.9

spread out on a pan in the open air. The crystals initially turned yellow, but on further irradiation became milky, so that the color was obscured. Samples were taken from time to time and placed in a closed tube, to which water was admitted after evacuation. The gas was not analyzed, but the volumes produced were measured, and the nitrite content of the solutions was determined. Results of the measurements are shown in Table I. Energy was not absorbed uniformly by the salt during the irradiation because of variation of thickness of the salt layer and its distribution on the pan with respect to the electron beam; the rate of energy dissipation was estimated as roughly 1.5 watts/g salt. Solutions of irradiated salt (0.01–0.07M) showed a pH of 9 to 10, and were thus more alkaline than can be accounted for by hydrolysis of nitrite.

At 25 watt-hr./g, about 21 percent of the nitrate had been converted to nitrite. The conversion rate decreased with time, suggesting that a steady state might eventually be reached after 40 percent or more conversion.

Qualitative experiments showed that gas evolution on solution was not greatly reduced by heating the irradiated salt below the melting point, but was entirely prevented by fusion of the irradiated salt. Presumably the gas came out during fusion, but no direct observation was made on this point. Irradiation lowered the melting point of the salt, presumably because of the admixture of nitrite.

Narayanswamy¹ has reported the formation of nitrite near the surface of nitrate crystals illuminated by light of wave-length 2200–2500Å. He ascribed the localization of the reaction at the surface to the escape of oxygen gas, assuming that recombination of the products should occur in the interior. In the present experiments, practically all the gas remained trapped in the crystal (as O atoms or O₂ molecules), so that thermal recombination must occur very slowly if at all. Localization of the photolysis must be ascribed to low penetration by the exciting light.

Existence of the photolysis has been ascribed¹ to dissociation of excited NO₃⁻ ions to NO₂⁻ ions and O atoms. Under electron bombardment, the same process probably occurs; in addition, many NO₃⁻ ions will be stripped of one outer electron, forming NO₃ radicals. This radical may later pick up an electron, with a probability of forming NO₂⁻ and O rather than NO₃⁻; or it may decompose thermally to NO₂ and O. The NO₂ may remain as such in the crystal, and hydrolyze on solution to HNO₂+HNO₃; or may pick up an electron to give nitrite ion. The small amounts of hydrogen gas and of alkali are ascribed to reaction with water of electrons which were trapped during

irradiation by barium ions, or at vacancies or imperfections in the crystal lattice.

The authors are pleased to acknowledge the help and counsel of Professor Milton Burton, in charge of radiation chemistry at the Metallurgical Laboratory when this work was performed, and Dr. F. J. Safford, in charge of operating the Van de Graaff generator.

* The work described herein was performed at the Metallurgical Laboratory of the University of Chicago under Contract No. W-7401-eng-37 with the Manhattan District.

¹ Narayanswamy, Trans. Farad. Soc. 31, 1411 (1935).

Structure for Soap Micelles as Indicated by a Previously Unrecognized X-Ray Diffraction Band*

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March 10, 1947

MEASUREMENTS on a previously unrecognized x-ray diffraction band B_M suggest that in an aqueous solution the micelle of a soap, or similar colloidal electrolyte, consists of only *one* double layer of soap molecules (Fig. 1). The subscript M designates that an associated spacing d_M measures the approximate thickness of the micelle. Over a range of concentrations of a given soap d_M is apparently constant and about twice the length of the particular molecule involved (Table I).

McBain has considered that soap micelles exist in spherical highly ionic and lamellar weakly ionic forms; whereas, Hartley has considered them as spherical only. Evidence for the lamellar micelle as a stack of double layers of soap molecules, with "bound" water between the double layers, seemed to be given by the x-ray work of Hess, Kiessig, Philippoff, *et al.* (1937–1942). Similar experimental results have been discussed in two papers^{1,2} from this laboratory in which extensive references to work on micelle structure are included.

It is now found that the spacing d_M' , associated with the new diffuse band, is essentially constant for any given soap, as it should be if it represents the thickness of the double layer. The thickness increases from 36.5Å for the 8-carbon atom soap to 58.1Å for the 16-carbon atom soap (Table I). This is an increase of 21.6Å caused by the addition of 16 C-atoms to the thickness of the double

TABLE I. Spacings in aqueous soap solutions calculated from the position of the peak of the micelle thickness band B_M .

Potassium soap	Bragg spacing ^a d_M ±1Å	2 × length of molecule $2l$	Modified Bragg spacing ^b d_M' ±1Å
Caprylate, KC ₈	29.7	30	36.5
Caprate, KC ₉	31.7	35	39.0
Laurate, KC ₁₂	35.3	40	43.4
Myristate, KC ₁₄	40.3	45	49.5
Palmitate, KC ₁₆	47.3	50	58.1
Sodium lauryl sulfate ^c	37.3	47	45.9

^a $d_M = \lambda / (2 \sin \theta)$, valid for many diffracting layers.

^b $d_M' = 1.23\lambda / (2 \sin \theta)$, valid in the limiting case for two diffracting centers (first maximum of $\sin x/x$). Note that $d_M < 2l < d_M'$ for the simple potassium soaps.

^c Kindly supplied by the Procter and Gamble Company.