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Radiolysis of Solid Nitrates

C. J. Hochanadel and T. W. Davis

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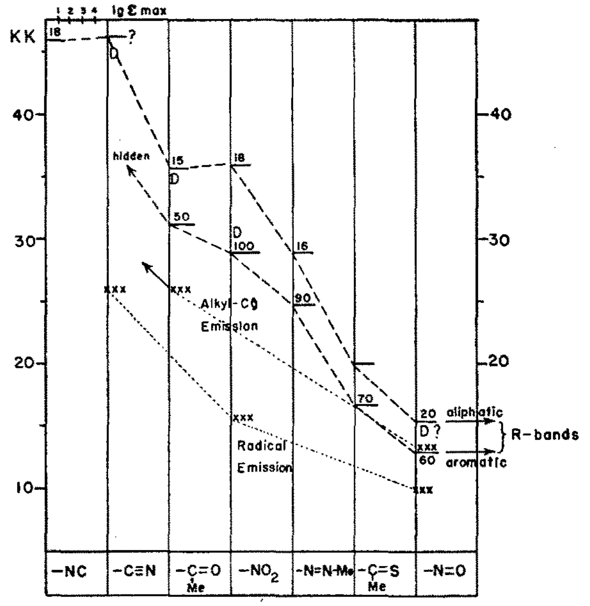

FIG. 3. *R* bands of CG's bound to alkyl, aryl, or the same CG (dimeride $=D$) and emission spectra of CG's bound to alkyl or as radicals.

which is exclusively based on alkyl or aryl derivatives of CG's. Figure 1 includes also spectra of additional CG's and phosphorescence bands which were not given in the earlier references.

Both in Figs. 1 and 2 the separation between phosphorescence bands and transitions II remains almost constant. This fact lends further support to Platt's[8] suggestion that an empirical relationship exists between these 2 types of transitions. A certain resemblance exists between Fig. 1 and Platt's figure for polyacenes[8] as far as the relative spectral positions of transitions I, II, III,[1] and the phosphorescence bands are concerned. This suggests a qualitative similarity between the conjugative effects of CG's on these spectra and the effects of aromatic annelation.

R bands of the dimeride and the alkylderivative of a CG apparently have similar frequencies (Fig. 3). The spectrum of the dimeride biacetyl is exceptional, for it shows 2 absorption bands with *R* band intensity. The higher one ($35kK$) fits into the regularities of the *R* bands of Fig. 3 and is, therefore, very probably the *R* band. The other one ($23kK$) is an unusual absorption band at a place where a very weak $T \leftarrow S$ band might be expected.[9]

R bands of a CG conjugated with $C=C$ or phenyl have probably almost identical frequencies and intensities.

The few phosphorescence data available for aliphatic compounds containing CG's suggest that the location of these emission bands approximately follows the trend of the *R* bands in Fig. 3.

Some CG's are known in their free state as radicals (CN, $COCH_3$, NO_2, NO). Emission spectra of these radicals are known. In one case, NO_2, also the absorption spectrum (*R* band, $25kK$)[10] has been recorded. Certain emission spectra of these radicals[11–13] follow the trend of the *R* bands in Fig. 3. The tendency of chromophoric radicals to dimerize appears to decrease in the order of the above given sequence of CG's.

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C. J. HOCHANADEL AND T. W. DAVIS*

Chemistry Division, Oak Ridge National Laboratory,† P.O. Box P, Oak Ridge, Tennessee.

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CRYSTALLINE inorganic nitrates decompose[1,2] on exposure to ultraviolet light with quantum yields which depend on the cation. The yields were related[2] to the field strength exerted by the cation on the nitrate ion, and were smallest for cations exerting the largest field strength. The sensitivities of potassium and sodium nitrates to decomposition by the radiations from a nuclear reactor[3] were in the same order as for ultraviolet light. The higher yield observed for the potassium salt was attributed[3] to the greater space available in the crystal. In attempting to further elucidate the factors determining the stability of the solid, the gamma ray-

TABLE I. Nitrite yields from the gamma-ray decomposition of solid nitrates.

Salt	Mass abs. coeff. $\frac{\mu-\sigma_s}{\rho}$	NO_2^- ions per 100 ev $G(NO_2^-)$	$G'(NO_2^-)$	Relative yields G_{rel}	G_{rel}'	ϕ_{rel}
$CsNO_3$	0.0246	1.68 ±0.05	4.55	1.0	1.0	1.0
KNO_3	0.0263	1.57 ±0.05	2.45	0.95	0.54	0.51
$NaNO_3$	0.0262	0.25 ±0.02	0.35	0.15	0.07	0.06
$LiNO_3$	0.0262	0.02 ±0.007	0.02	0.012	0.004	0.01
$AgNO_3$	0.0257	0.20 ±0.05	0.50	0.12	0.1	0.19
$Ba(NO_3)_2$	0.0250	1.88 ±0.15	3.68	1.12	0.81	0.25
$Pb(NO_3)_2$	0.0319	0.44 ±0.04	1.05	0.26	0.23	0.19
$La(NO_3)_3$	0.0255	1.5 ±0.2	2.50	0.91	0.55	0.22
$La(NO_3)_3 \cdot 6H_2O$	0.0258	2.5 ±0.3	5.6	1.52	1.23	0.63
			3.25[a]		0.71	

[a] *G* divided by the fraction of electrons in the NO_3^- ions plus H_2O.

induced decomposition of a series of nitrates has been studied.

The cp nitrates were ground, dried at 100°C, and then irradiated either in the presence of air, or under vacuum after degassing. The air had no effect on the yields. The salts were irradiated with cobalt gamma rays at a dose rate of about 1.5×10^{17} ev, g^{-1}, min^{-1}. After irradiation, the salts were dissolved in water and the nitrite determined by the color developed with dimethyl-α-naphthylamine-sulfanilic acid reagent. The molar extinction coefficient at 5350 A was 431. Since the principal products produced in the solid are nitrite and oxygen[2–5] the gaseous products were not analyzed. The determination of dosage was based on ferrous sulfate dosimetry, taking the 100-ev yield of ferric ion to be 15.6.[6] The calculation of total energy absorbed in the nitrates was based on the "true" mass absorption coefficients[7] listed in Table I. Nitrite production was linear with dose in the range studied (usually up to 5×10^{20} ev, g^{-1}), and, therefore, back reaction was negligible. The 100-ev yields of nitrite are listed in Table I. The G' values are the G values divided by the ratio of electrons in the nitrate ion to the total number in the salt. In this assessment of the fraction of energy absorbed by the nitrate ion, no correction was made for the differences in electron stopping powers of the various electrons. Relative values of G and G' along with relative quantum yields,[2] ϕ_{rel}, appear in the last columns.

In a general way, the yields for decomposition induced by gamma rays follow the same order as for ultraviolet light, indicating that the same processes determine the stability in the two cases. Assuming the dissociation of excited nitrate ions (formed either directly or by capture of an electron by NO_3) into NO_2^- and O as suggested by Allen and Ghormley,[4] the O atom might then: (a) recombine with the NO_2^- ion produced simultaneously; (b) react with an adjacent NO_3^- ion to form NO_2^- and O_2, or (c) diffuse through the lattice until it reacts with another O atom, NO_2^-, or O_2. The linear production of NO_2^- with dose indicates little back reaction of O atoms which escape initial recombination, and hence rules against (c). Also, the low absolute quantum yields (0.002 to 0.2), and the similarity in relative stability toward ultraviolet light and high energy radiation, indicate that the decomposition can best be explained by a competition between (a) and (b), the relative amounts of each depending on the salt. The fact that ϕ and G' show somewhat better agreement than ϕ and G suggests that the energy imparted to the cation electrons is less effective in causing nitrate decomposition than the energy imparted to the nitrate electrons and to the electrons in water of hydration.

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[*] Summer participant in 1954 on leave from New York University, University Heights, New York 53, New York.

[†] Operated for the U. S. Atomic Energy Commission by Union Carbide Nuclear Company.

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