From the results of various studies carried out in these laboratories,[4] a number of 2- and 3-substituted 1,1-dinitroalkanes and 3-substituted 1,1-dinitro-2-alkene salts were obtained. During the course of these investigations, the infrared spectra of some of these salts were determined and used in characterization. These results, as well as the spectra of a number of previously unreported substituted 1,1-dinitrocarbanion salts, are summarized in Table I.

TABLE I

NITRO GROUP ABSORPTION OF 1,1-DINITROCARBANION SALTS

$^-C(NO_2)_2Y$, Y =	Infrared bands 1100-1200 cm.$^{-1a}$	 1200–1300 cm.$^{-1}$
$-CH_2CHOHCO_2CH_3$	1165 (1130)	1262
$-CH{=}CHCO_2CH_3$	1182	1268
$-CH_2CH_2CO_2CH_3$	1165 (1120)	1245
$-CH_2CHOHCONH_2$	1175 (1132)	1273
$-CH{=}CHCONH_2$	1165	1267
$-CH_2CH_2CONH_2$	1165 (1115)	1260
$-CH_2CHOHCOO^-$	1165 (1115)	1270
$-CH_2CH_2COO^-$	1180 (1112)	1255
$-CH{=}CHNO_2$	1185	1255
$-CH_2CH_2NO_2$	1182 (1140)	1272
$-CH{=}CHCN$	1176	1268
$-CH_3CN$	1190 (1112)	1268
$-CH_2CHOHCOCH_3$	1160 (1120)	1268
$-CH_3$	1150	1240
$-(CH_2)_3CH_3$	1187 (1120)	1248

[a] Values in parentheses represent a second band of about equal or lower intensity.

From the data in Table I, the empirical assignments given to the two bands for the nitro group in substituted 1,1-dinitrocarbanion salts are 1173 ± 10 and 1269 ± 9 cm.$^{-1}$, with maximum deviations of 23 and 22 cm.$^{-1}$, respectively. In most of the saturated derivatives, a second band of about equal or somewhat lower intensity appears in the 1100–1200-cm.$^{-1}$ region. This value is given in parentheses. These bands were not used in the average since they are generally absent in the unsaturated derivatives.

By analogy with the covalent nitro compounds,[1] the 1173-cm.$^{-1}$ band would be due to the symmetrical stretching mode and the 1262-cm.$^{-1}$ band would be due to the asymmetrical stretching mode of the nitro group. This shift in the value of $\nu_{\max}$ to lower frequencies as compared to the covalent nitro compounds[1] would be expected due to the resonance interaction of the carbanion with the nitro groups.

Experimental

The potassium salts were prepared as described previously.[4] *Extreme caution was exercised in grinding the samples for mull preparation as all of these salts are extremely sensitive to impact and/or friction and may explode during this operation.* Infrared spectra were determined on mulls in Nujol using a Beckman IR-4 spectrophotometer. Individual values of $\nu_{\max}$ in Table I have an average deviation of 5 cm.$^{-1}$.

Acknowledgment.—This work was supported by the Foundational Research Fund of the U. S. Naval Ordnance Laboratory, Task FR-44.

[4] M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961); M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961); L. A. Kaplan and M. J. Kamlet, *ibid.*, **27**, 780 (1962); M. J. Kamlet and L. A. Kaplan, *ibid.*, **28**, 2128 (1963); L. A. Kaplan, unpublished results.

Solvolytic Deoxymercuration Catalyzed by Iodide Ion[1]

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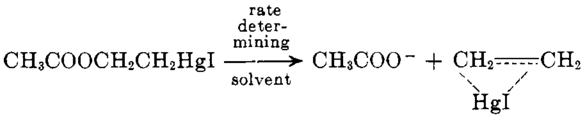
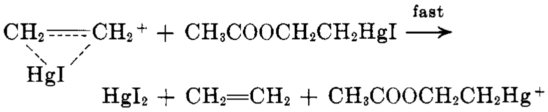
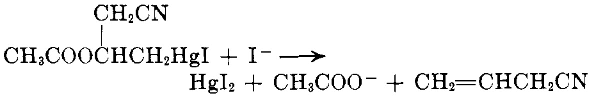
In a previous publication[2] 2-acetoxyethylmercuric iodide has been shown to undergo a solvolytic deoxymercuration, shown in eq. 1 and 2. Acid-catalyzed deoxymercuration has been shown[3] to be subject to cocatalysis by one or two iodide ions,[3] and similar cocatalysis might be expected for solvolytic deoxymercuration. It has now been found in dilute, aqueous solution, for the reaction whose over-all course is shown in eq. 3. This completes the H$^+$–I$^-$ deoxymercuration system, in the sense that catalysis by zero or one proton; zero, one, or two iodide ions; and all combinations thereof, has now been observed in dilute, aqueous solution. Acid catalysis of the reaction shown in eq. 3 has also been found, but is shown to be insignificant at the pH of the iodide-catalyzed solvolysis.



$$CH_3COOCH_2CH_2HgI \xrightarrow[\text{solvent}]{\text{rate determining}} CH_3COO^- + \underset{HgI}{CH_2\overset{}{=\!=}CH_2^+} \quad (1)$$



$$\underset{HgI}{CH_2\overset{}{=\!=}CH_2^+} + CH_3COOCH_2CH_2HgI \xrightarrow{\text{fast}} HgI_2 + CH_2{=}CH_2 + CH_3COOCH_2CH_2Hg^+ \quad (2)$$



$$CH_3COO\overset{CH_2CN}{\overset{|}{C}}HCH_2HgI + I^- \longrightarrow HgI_2 + CH_3COO^- + CH_2{=}CHCH_2CN \quad (3)$$

Results

Reactions were carried out at 25°, in aqueous solution containing $<2\%$ of methanol. (The substrate was handled as a stock solution in methanol.) Potassium iodide was the source of iodide ion and the acid, where used, was perchloric acid.

The progress of the reaction was followed by following the buildup of the ultraviolet absorption spectrum of HgI_2 and/or its iodide ion complexes, as previously described.[2-4] Substrate concentrations were in the range 10^{-4}–10^{-5} *M* and the iodide ion, when added, was always in at least tenfold excess, so that a first-order rate law was obeyed within each experiment. The integrated form of the first-order rate law, eq. 4, was

$$k_1' = \frac{2.303}{(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \quad (4)$$

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[1] This work was supported by the Air Force Office of Scientific Research through Grant AF-AFOSR-16-63. Reproduction is permitted for any purpose of the U. S. government.

[2] M. M. Kreevoy and G. B. Bodem, *J. Org. Chem.*, **27**, 4539 (1962).

[3] M. M. Kreevoy, R. A. Kretchmer, G. E. Stokker, and A. K. Ahmed, *ibid.*, **28**, 3184 (1963).

[4] M. M. Kreevoy, *J. Am. Chem. Soc.*, **81**, 1099 (1959).

used, except for experiments in which no iodide ion was added. In those, an additional factor of 2 appears, in the denominator, on the right hand side of eq. 4.[4] The pseudo-first-order rate constant is k_1'; the optical density is D; time is t; the time at which an optical density was measured is subscripted.

The first-order rate law was very closely obeyed for the 2–3 half-lives that were observed in most experiments, and no systematic deviations were observed. Rate constants were evaluated graphically from plots of log $(D_t - D_\infty)$ *vs.* t. Previous experience[2-4] has shown that such rate constants have a reproducibility of ~ ±5%, and this was confirmed by repeating most of the experiments here reported. Values of k_1' are shown, as a function of iodide concentration, in Table I.

TABLE I

RATE CONSTANTS AS A FUNCTION OF $[I^-]$

$10^4[I^-]$, M	$10^4\ k_1'$ sec.$^{-1}$	$10^4\ k_1'$ sec.$^{-1}$, calcd.[b]
0.00[a]	0.50	
2.03	1.73	2.05
4.06	4.07	3.66
12.2	12.1	10.6
20.3	19.3	18.5
40.6	36.1	42.1
40.6[a]	36.1	42.1
81.2	90.4	105.6
81.2[a]	89.6	105.6
101	144	144
122	218	192

[a] Run in the presence of $6.4 \times 10^{-3}\ M$ acetic acid and $1.37 \times 10^{-3}\ M$ sodium acetate. [b] Calculated from eq. 5.

To test the hypothesis that these rate constants are pH independent in near neutral solutions, several were measured in acetic acid–acetate buffer solutions of pH ~4. These should differ by about 2 pH units from those in which no buffer was added. These values of k_1' are also shown in Table I. Within experimental error no change in k_1' could be observed.

The data in Table I were fitted to eq. 5. The value

$$k_1' = k_1 + k_2\,[I^-] + k_3\,[I^-]^2 \tag{5}$$

$$k_1 = 5.0 \times 10^{-5}\ \text{sec.}^{-1}$$
$$k_2 = 0.75\ \text{l. mole}^{-1}\ \text{sec.}^{-1}$$
$$k_3 = 67\ \text{l.}^2\ \text{mole}^{-2}\ \text{sec.}^{-1}$$

of k_1 was obtained directly from k_1' measured in the absence of iodide ion. Values of k_2 and k_3 were obtained by the iterative process previously described.[3] The values of k_1' calculated from eq. 5 are shown, for comparison, along with the experimental values, in Table I. In several cases, the difference between the two is somewhat larger than the expected experimental error, but it is not systematic and does not seem to call eq. 5 seriously into question. The derived values of k_2 and k_3 are probably uncertain by about 10–15%, k_2 being somewhat more reliable than k_3. There is no question about the reality of k_3, however. At the highest iodide concentration, k_1' is larger than would be predicted by any reasonable values of k_1 and k_2 alone by about a factor of two, and is increasing, roughly, as the square of the iodide concentration.

For comparison the rate coefficient for acid catalysis, k_2^H, was also obtained, by applying eq. 6 to the k_1 values obtained in the absence of iodide ion. (The k_1 of eq. 6 is the same as that cited above.) The value of

$$k_1' = k_1 + k_2^H \tag{6}$$

1.72×10^{-3} l. mole^{-1} sec.$^{-1}$ was obtained for k_2^H from four determinations of k_1' with perchloric acid concentrations ranging up to 0.6430 M. The average deviation from the mean was 0.05×10^{-3} l. mole^{-1} sec.$^{-1}$.

Discussion

Deoxymercuration induced by halide ions alone has been previously suggested,[5-7] but the details of the kinetics do not seem to have been worked out. The present work fills in the last gaps in the H^+–I^- deoxymercuration scheme, demonstrating catalysis of the neutral solvolysis by one or two iodide ions.

As before,[3] the ratios k_2/k_1 and k_3/k_2 have the form and the significance of the first and second complexing constants of the transition state for the uncatalyzed reaction with iodide ion, as shown in eq. 7 and 8.

$$\frac{k_2}{k_1} = \frac{(*_2)}{(*_1)[I^-]} \tag{7}$$

$$\frac{k_3}{k_2} = \frac{(*_3)}{(*_2)[I^-]} \tag{8}$$

(The subscript indicates the number of iodide ions contained by the particular transition state, $*_n$.)

The ratio k_2/k_1 is 1.5×10^4 l. mole^{-1} and k_3/k_2 is 90 l. mole^{-1}. In order of magnitude these are similar to the ratios (3.2×10^3 l. mole^{-1} and 34 l. mole^{-1}) previously reported[3] (with a somewhat different substrate structure) for acid deoxymercuration. This suggests that the immediate environment of the mercury atom is similar in the two reactions, as these complexing constants are sensitive to this environment. (The formation constants of HgI_2, HgI_3^-, and HgI_4^{-2} from HgI^+, HgI_2, and HgI_3^-, respectively, are 10^{11}, 10^4, and 10^2 l. mole^{-1}.[8]) This similarity is in accord with the similar transition states that have been suggested for the two reactions.[2,9]

Both k_1 and k_2^H here reported are about an order of magnitude smaller than the similar quantities for (2-iodomercuriethyl) acetate.[2,10] This is in qualitative accord with the effect expected of the electron-withdrawing cyanomethylene group.[11]

Experimental

2-Acetoxy-3-cyanopropylmercuric Iodide.—This compound was prepared by exchange from 2-acetoxy-3-cyanopropylmercuric chloride. The latter was made from 3-cyanopropene, (Matheson Coleman and Bell, practical) by the general method of Ichikawa, Onchi, and Araki.[12] It was not isolated. Its chloroform solution was washed repeatedly with dilute aqueous potassium iodide and then with water, and dried over calcium sulfate; the solvent was evaporated under vacuum for 15 hr. The product was a light yellow, uncrystallizable, undistillable oil, but had a suitable infrared spectrum.

Anal. Calcd. for $C_6H_8HgINO_2$: C, 15.88; H, 1.76. Found: C, 16.08; H, 1.86.

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