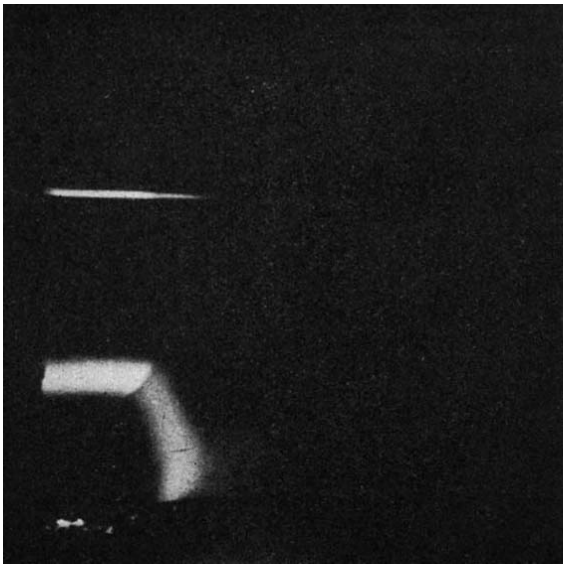

Fig. 2. Detonation through normal (top) and shocked nitromethane

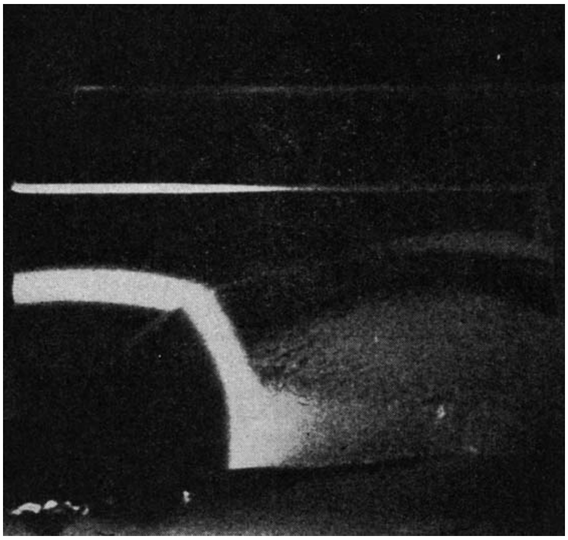

Fig. 3. Interaction between detonation wave fronts in nitromethane

(detonation rate 7,600 m/sec), which drove a wiping shock wave into the nitromethane through the 1/8-in. aluminium tank floor. This shock was insufficient to initiate nitromethane directly but did so after reflexion from the opposite corner of the tank.

The event was recorded on Eastman 'H.S. Ektachrome' film. The film showed the normal bright yellow detonation proceeding upward into the unshocked liquid and a dim yellow, right-going, zone in the compressed explosive which maintained its identity throughout the sequence. The experiment was reproducible. Although the zones were easily distinguishable on colour film the brightness differences were not great and show to less advantage in black-and-white. An early frame is shown in Fig. 2. Fig. 3, from the same sequence, was contrast-controlled during printing to show details of the window break-up and the interaction line behind the wave fronts. The interaction line remained visible for some time and was, perhaps, etched into the 'Plexiglas' window. Campbell *et al.*[2] postulate a super-velocity detonation through the compressed region to explain the first dim light which they observed. In view of these experiments, it seems reasonable to attribute weak detonation light to the reaction of compressed material. Although there is some tendency for the wave in the compressed explosive to pull away from the normal front, it is not pronounced. Compression to higher densities would be expected to increase that tendency.

The photographs shown were taken without external illumination. Similar experiments, which were illuminated with diffused backlight from an argon flash bomb, showed the compressed but undetonated nitromethane to be transparent while everywhere behind the two detonation fronts a black, opaque, reaction product cloud had formed. We believe the opacity was due to free carbon from this oxygen-deficient explosive rather than opaquing of the 'Plexiglas' for two reasons: (1) explosives having transparent reaction products have been used and in these cases the 'Plexiglas' windows transmitted backlight; (2) experiments with front-lighted nitromethane tanks, having white grid lines painted on the inside front surface of the 'Plexiglas' window, have shown that such grid lines remained clearly visible after passage of the detonation wave. The lines remained visible until break-up of the window occurred.

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[1] Johansson, C. H., and Sternhoff, L., *Nature*, **183**, 247 (1959).
[2] Campbell, A. W., Davis, W. C., and Travis, J. R., *Phys. Fluids*, **4**, 498 (1961).
[3] Mallory, H. D., and McEwan, W. S., *J. App. Phys.*, **32**, 2421 (1961).

RADIATION CHEMISTRY

The Effect of *p*H on the Radical Yields in the γ-Radiolysis of Aqueous Systems

It is customary to describe the state of affairs about 10^{-8} sec after the passage of a fast electron traversing a liquid aqueous medium by equation (1):

$$G_{-H_2O}H_2O \rightsquigarrow G_{'H'}\,\text{'H'} + G_{OH}\,OH + G_{H_2}\,H_2 + G_{H_2O_2}\,H_2O_2 \quad (1)$$

in which $G_{'H'}$ and G_{OH} are the numbers of H atoms and OH radicals respectively which are available to react with solutes for each 100 eV energy deposited in the water. Recent work[1,2] has shown that the precursor of the hydrogen atom is a solvated electron, e^-_{aq}, capable of reaction in this form with solutes such as N_2O[3], $ClCH_2COOH$[4], O_2[2], H_2O_2[2], etc. The solvated electron is also able to react with hydrogen ions according to equation (2), when it is converted into a hydrogen atom:

$$H^+_{aq} + e^-_{aq} \longrightarrow H_{aq} \quad (2)$$

Consequently, as the *p*H of a solution is reduced a solute has less chance of reaction with e_{aq} and more of reacting with H. It is also known[3] that reduction of the *p*H below $\sim$ 3 causes the production in equal yield of two additional entities, stoichiometrically equivalent to H and OH and tentatively identified as H_2^+ and OH. The fact that the molecular yields,

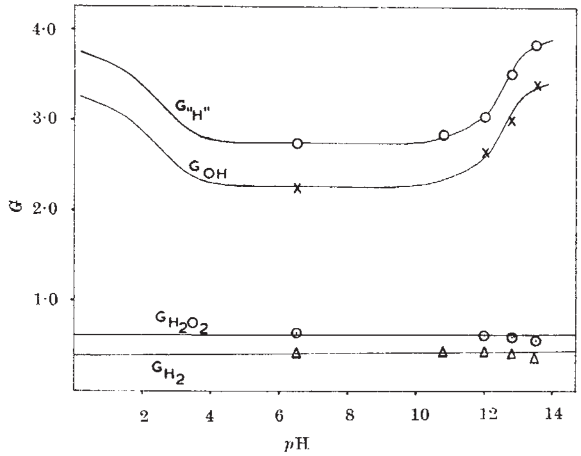

Fig. 1. Variations with pH of $G_{\cdot H'}$, G_{OH}, G_{H_2} and $G_{H_2O_2}$ for γ-irradiated liquid aqueous systems. Lines at pH < 6 based on many previous investigations (see Fig. 9, ref. 3). Lines at pH > 6 based on the $Fe(CN)_6^{3-}$ — $Fe(CN)_6^{4-}$ — N_2O system described here and to which the experimental points refer

G_{H_2} and $G_{H_2O_2}$ do not diminish as the *p*H is reduced below 3, indicates that these entities are formed by the attack of the acid on some intermediate which otherwise (that is, at *p*H > 3) reverts to water, and the kinetics[3] indicate that the reversion is first order in intermediate concentration. This intermediate may be either an excited water molecule, H_2O*, or an isolated radical pair in a solvent cage, denoted by (H + OH). Its reaction with the acid is then represented by either equation (3) or (4):

$$H_2O* + H^+_{aq} \longrightarrow H^+_{2\,aq} + OH_{aq} \quad (3)$$

$$(H + OH) + H^+_{aq} \longrightarrow H^+_{2aq} + OH_{aq} \quad (4)$$

Consequently, the conventional hydrogen atom yield $G_{\cdot H'}$ is the composite quantity, $G_{e^-} + G_H + G_{H_2^+}$. The dependence of $G_{\cdot H'}$. G_{OH}, G_{H_2} and $G_{H_2O_2}$ on *p*H below *p*H 7 is shown in the left hand part of Fig. 1.

$$H_2O* + OH^-_{aq} \longrightarrow e^-_{aq} + OH_{aq} \quad (5)$$

$$(H + OH) + OH^-_{aq} \longrightarrow e^-_{aq} + OH_{aq} \quad (6)$$

We may envisage the reactions (5) and (6), which are the basic analogues of reactions (3) and (4), and we are therefore led to expect a perceptible increase of the conventional yields as the *p*H is increased above about 11. Satisfactory solutes for use in alkaline solutions are rare and we have therefore tackled this problem in the following manner. First, we have shown that when acrylamide is used as a solute $G(H_2) = G_{H_2}$ and $G(H_2O_2) = G_{H_2O_2}$ undergo no sudden changes between *p*H 0 and 13. Secondly, we have shown that the only reactions occurring at *p*H > 7 in deaerated aqueous solutions containing potassium ferrocyanide, potassium ferricyanide and varying amounts of nitrous oxide are:

$$Fe(CN)_6^{3-} + e^-_{aq} \longrightarrow Fe(CN)_6^{4-} \quad (7)$$

$$N_2O + e^-_{aq} \longrightarrow N_2 + O^-(\rightarrow OH) \quad (8)$$

$$OH + Fe(CN)_6^{4-} \longrightarrow OH^- + Fe(CN)_6^{3-} \quad (9)$$

$$H_2O_2 + 2Fe(CN)_6^{3-} \longrightarrow 2H^+ + O_2 + 2Fe(CN)_6^{4-} \quad (10)$$

Hence, for this system, we obtain the radical and molecular yields from equations (11)–(14) inclusive, in which the superscript, $-N_2O$, means no N_2O present and the superscript, $+N_2O$, means that the N_2O concentration is sufficiently large for $k_8[N_2O] \gg k_7[Fe(CN)_6^{3-}]$.

$$G_{H_2O_2} = G(O_2) \quad (11)$$

$$G_{H_2} = G(H_2) \quad (12)$$

$$G_{\cdot H'} = G(N_2)^{+N_2O} \text{ or } \{G(\text{ferri})^{+N_2O} - G(\text{ferri})^{-N_2O}\}/2 \quad (13)$$

$$G_{OH} = G_{\cdot H'} + 2\,G_{H_2} - 2G_{H_2O_2} = \{G(\text{ferri})^{+N_2O} + G(\text{ferric})^{-N_2O} + 4\,G(O_2)\}/2 \quad (14)$$

The values of these yields are shown in the right-hand half of Fig. 1, and their variation with *p*H is in accord with the proposed existence of reaction (5) or (6). At *p*H ⩽ 6 reaction (10) is replaced by the relatively slow reaction (15):

$$2\,Fe(CN)_6^{4-} + H_2O_2 \rightarrow 2\,Fe(CN)_6^{3-} + 2\,OH^- \quad (15)$$

so that the measurement of the post-irradiation reaction and of the effect of N_2O on G(ferri) can be used to determine the radical and molecular yields. The values at *p*H = 6 are shown in Fig. 1.

Two other pieces of evidence support this hypothesis. Thus, Dainton and Peterson[3] showed that $G(N_2)$ from γ-irradiated aqueous solutions of N_2O undergoes an increase of about one unit as the *p*H is increased above 11. This was attributed to ionic dissociation of the OH radical, but this explanation is less free from objection than the simple assumption of the occurrence of either reaction (5) or reaction (6). Again, the existence of the acid-base reaction (16), which is closely related to reactions (5) and (6) and was first proposed by Baxendale and Hughes[5], has recently been unequivocally demonstrated[6]:

$$H_{aq} + OH^-_{aq} \longrightarrow e^-_{aq} \quad (16)$$

If H^+ and OH^- ions can each react with H_2O* or (H + OH) it is to be expected that other solutes will exist which also have this property. In fact aqueous solutions of some solutes at a *p*H within the range 3 < *p*H < 11 on irradiation give a single product which seems to be derived from reaction of the solute with e^-_{aq} alone, while solutions of other solutes give products seemingly derived from reactions with both e^-_{aq} and H. This situation is readily explicable. A solute, such as nitrous oxide, may react rapidly with e^-_{aq} but only slowly with (H + OH) or H_2O* and will therefore 'see' only e^-_{aq}. Another solute may react rapidly with (H + OH) or H_2O* as well as with e^-_{aq} but in reacting with the former generates a product which is converted back to the original reagent by the remaining radical of the radical pair. Examples of this may be oxygen and $Fe(CN)_6^{3-\text{and}4-}$ when the relevant fast reactions are:

$$H_2O* \text{ or } (H + OH) + O_2 \rightarrow HO_2 + HO \rightarrow H_2O + O_2$$

$$H_2O* \text{ or } (H + OH) + Fe(CN)_6^{3-} \rightarrow H_2O^+ \text{ or } H^+ + OH + Fe(CN)_6^{4-} \rightarrow H_2O + Fe(CN)_6^-$$

$$H_2O* \text{ or } (H + OH) + Fe(CN)_6^{-4} \rightarrow H + OH^- + Fe(CN)_6^{-3} \rightarrow H_2O + Fe(CN)_6^{-4}$$

The solute in this case may be regarded as a quencher of H_2O* or as a catalyst of H + OH recombination but in any event will only 'see' e^-_{aq} or OH. There are yet other solutes which can react quickly with e^-_{aq} to form one product and with H_2O* or (H + OH) to form another which is resistant to attack by the conjugate radical. These will 'see' both e^-_{aq} and H_2O* or (H + OH). An example is Cl CH_2COOH, which reacts with e^-_{aq} to form Cl^- ($G(Cl^-)$ at 4 < *p*H < 7 = ∼ 3) and with H_2O* or (H + OH) to form H_2($G(H_2)$ at 4 < *p*H < 7 = ∼ 1)[4,7], which reacts only slowly with OH. Such solutes should compete with OH^- ions for H_2O* or (H + OH) and accordingly we expect that for several organic solutes $G(H_2)$ should decrease markedly around pH 11 and G (product derived from e_{aq}^-) show a complementary increase.

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[1] Collinson, E., Dainton, F. S., Smith, D. R., and Tazuké, S., *Proc. Chem. Soc.*, 140 (1962).
[2] Czapski, G., and Schwarz, H. M., *J. Phys. Chem.*, **66**, 471 (1962).
[3] Dainton, F. S., and Peterson, D. B., *Proc. Roy. Soc.*, A, **267**, 443 (1962).
[4] Hayon, E., and Weiss, J. J., *Proc. Second Conf. Peaceful Uses Atomic Energy, Geneva*, **29**, 80 (1958).
[5] Baxendale, J. H., and Hughes, G., *Z. phys. Chem.*, N.F., **14**, 323 (1958).
[6] Jortner, J., and Rabani, S., *J. Amer. Chem. Soc.*, **83**, 4868 (1961).
[7] Allen, A. O., and Hayon, E., *J. Phys. Chem.*, **65**, 2181 (1961).

CHEMISTRY

Complex Formation of Monomeric Amides with Lithium Perchlorate

It has been demonstrated that aqueous solutions of lithium bromide can induce the disruption of the ordered portions of fibrous and globular proteins[1–4]. Since this phenomenon is observed for proteins of widely differing secondary and crystallographic structure and also amino-acid composition, the conclusion was reached that an interaction with the peptide linkage was involved. The nature of the melting temperature–LiBr concentration curve for both α and β keratin[1,2] suggested that, in addition, an alteration in the nature of the peptide bond occurs.

Lithium bromide and similar salts are known to form complexes with simpler compounds containing some of the characteristic features of the peptide groups[5–9]. In particular, complexes of the general formula $LiX.nCO(NH_2)_2$ with $n = 1$, 2, and 3 have been established for aqueous solutions of lithium bromide or lithium chloride with urea[7,8]. A similar situation has also been demonstrated for aqueous solutions of lithium bromide with either *N*-methylacetamide or dimethylacetamide[9]. Contrary explanations have been offered, and the interpretation of the results is complicated by the necessity of having a third component, water, present in the systems previously selected for study. Since the melting of the fibrous proteins can also be demonstrated in non-aqueous solutions of lithium bromide[10], the examination of model compounds to elucidate the nature of the interaction is best accomplished by the elimination of water from the system.

To this end we have investigated, by means of an infra-red spectroscopic technique, the interaction of anhydrous lithium perchlorate with *N*-methylpropionamide (NMP). Solutions of the anhydrous salt and NMP were prepared in a dry nitrogen atmosphere; the molar ratio of amide to lithium employed was approximately 3 : 1. This system, thus, possesses the advantage that adequate solubility of the salt in the amide can be obtained without the intervention of water.

The spectral data for the pure amide and the solution are illustrated in Fig. 1. A strong interaction between the lithium salt and the amide group is indicated. Lithium bromide was found to give essentially the same results, so the effect can be attributed largely to the lithium ion. The amide absorption band at 1,645 cm^{-1} attributed to C=O stretch (amide I) shows a marked change on addition of lithium perchlorate to the pure amide. This carbonyl frequency is lowered in wave number; the single band observed with the pure amide (1,645 cm^{-1}) becomes a doublet (1,645 cm^{-1} and 1,620 cm^{-1}). The amide absorption band at 1,550 cm^{-1} attributed to N—H deformation coupled with C=N stretch (amide II) (ref. 11), and its accompanying weaker absorption band (amide III), are slightly changed on addition of lithium perchlorate to the pure amide.

The N—H stretching mode at 3,300 cm^{-1} of pure NMP is also significantly altered on addition of lithium perchlorate. The strong band at 3,300 cm^{-1} is completely replaced by a strong band at 3,400 cm^{-1}, representing a change toward the higher frequency by 100 cm^{-1}. In addition, the weaker NH vibrational band observed in the pure amide at 3,100 cm^{-1} becomes of even weaker intensity, almost to disappearance, in the lithium perchlorate–amide mixture.

These results are strikingly similar to those obtained by Gerrard, Lappert, Pyzora and Wallis[12] in their investigation of the spectra of simple amides and the complexes that are formed with boron trihalides. The results reported here can be interpreted in a similar manner. The results suggest that the lithium ion interacts with the carbonyl group directly, rather than with the nitrogen atoms previously suggested for the urea complexes of lithium chloride[7]. The splitting of the carbonyl frequency may be attributed to lithium to carbonyl bonding, the lithium ion being bonded perhaps to more than one carbonyl group:

$$C=O \ldots Li^{+} \ldots O=C \quad \text{or} \quad \begin{array}{c} C \\ \| \\ O \\ \vdots \\ C=O \ldots Li^{+} \ldots O=C \end{array}$$

A somewhat similar conclusion has recently been reached by Bello and Bello[13] from a preliminary

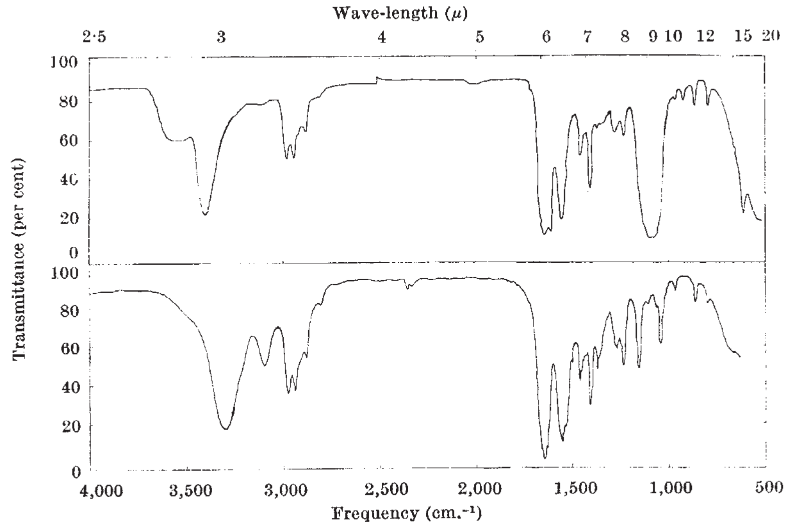

Fig. 1. Upper curve, infra-red spectrum of pure *N*-methylpropionamide; lower curve, infra-red spectrum of anhydrous lithium perchlorate–*N*-methylpropionamide solution