PHYSICAL CHEMISTRY

N. A. BAKH, M. RODER, L. T. BUGAENKO

1963

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

N. A. BAKH, M. RODER, L. T. BUGAENKO

MECHANISM OF RADIATION OXIDATION AND REDUCTION OF INORGANIC ACCEPTORS IN ACETONE SOLUTIONS

(Presented by Academician A. N. Frumkin, January 5, 1963)

In studying the action of ionizing radiation on dilute solutions of methylene blue (MB) and its leuco base (LMB) in various organic liquids, it was established that, in contrast to a number of solvents in which the oxidation of LMB and the reduction of MB are characterized by yields G of 2 to 4 molecules/100 eV, in acetone $G(-\text{LMB}) = G(\text{MB})$ reaches 12-13 molecules, i.e., requires ~ 25 eV/100 eV (1,2). Such a high value makes untenable the interpretation given for the first group of solutions, according to which the reactions are carried out by free radicals arising during radiolysis of the solvents as a result of ionization acts, as in aqueous solutions. In order to determine whether the special behavior of acetone is retained with respect to other oxidation-reduction acceptors, the action of X-radiation on solutions of ions of variable valence was studied: Fe^{III}, Fe^{II}, Cu^{II}, Cu^{I}, Cr^{VI}, Cr^{III}, Mn^{VII}, J$^-$, and J$_3^-$.

In the case of cations the corresponding chlorides were used; in the case of anions, CrO_3, $KMnO_4$, and KJ. Without irradiation the solutions are stable in the absence of oxygen. Irradiation of 10^{-5}–10^{-2} M solutions, sealed in vacuum or in a nitrogen atmosphere, was carried out in cells that made it possible to determine the concentration spectrophotometrically without exposing the solution to air. Details of the experiment and of the preparation of the samples are described elsewhere.

In solutions of ions that before irradiation are in the higher valence state, reduction occurs in all cases upon irradiation, regardless of whether only electron transfer is required or also rupture of oxygen bonds.

Fig. 1. Dependence of the reduction yield of Cu^{II} (1), Fe^{III} (2), and Cr^{VI} (3) on concentration during irradiation of acetone solutions.

Figure 1 shows the dependence of the radiation yield on the concentration of the acceptor for Cu^{II}, Fe^{III}, and Cr^{VI}. As can be seen, the reduction yields increase with concentration and at 10^{-3}–10^{-2} M reach constant values of 17.3, 14.5, and 10.5 equiv/100 eV, respectively. In this concentration region the reactions are undoubtedly due to products of radiolysis of the solvent, and not to the direct

Figure 2

Figure 1: Figure 2

Figure 3

Figure 2: Figure 3

action of radiation on the acceptor. The absence of post-radiation effects with far from complete consumption of the acceptor in solutions of $CuCl_2$, $FeCl_3$, and CrO_3 shows that the reactions are carried out by short-lived, and not stable, products of acetone radiolysis.

In contrast to Cu^{II}, Fe^{III}, and Cr^{VI}, in the reduction of Mn^{VII} to Mn^{IV} a significant post-radiation effect is observed. Additional reduc-

reduction of $\mathrm{Mn}^{\mathrm{VII}}$ corresponds, at each dose, to the amount of the molecular products formed that are capable of carrying out this reaction. Since the rate of post-radiation reduction is an order of magnitude lower than the rate of reduction during irradiation, the latter must here also be determined by short-lived products of radiolysis. Figure 2 presents the dependences on the concentration of $\mathrm{KMnO_4}$ of the yields of reduction of $\mathrm{Mn}^{\mathrm{VII}}$ during irradiation (curve 1) and of the total reduction, including the aftereffect (curve 2). The value $G(-\mathrm{MnO}_4^-) = 20$ equiv/100 eV attained in our experiments in a $2 \cdot 10^{-3}\ M$ solution was still not limiting. The difference curve 3 corresponds to the yield of molecular products. The increase in $G(-\mathrm{MnO}_4^-)_{\mathrm{irr}}$ with increasing acceptor concentration, accompanied by a simultaneous decrease in $G(-\mathrm{MnO}_4^-)_{\mathrm{mol}}$, shows that short-lived primary radiolysis products participate in competing reactions of reduction of $\mathrm{Mn}^{\mathrm{VII}}$ and formation of molecular products from acetone.

Fig. 2. Effect of $\mathrm{KMnO_4}$ concentration on the yield of radiation reduction of $\mathrm{Mn}^{\mathrm{VII}}$ and formation of molecular products during irradiation of acetone solutions

Oxidation of inorganic ions is observed considerably less often than reduction upon irradiation of acetone solutions in the absence of oxygen. Of all the acceptors investigated, only $\mathrm{Fe}^{\mathrm{II}}$ is oxidized under these conditions. Characteristic effects are observed in KJ solutions. In the absence of O_2, iodine is not formed during irradiation, but appears only after it is stopped, as shown in Fig. 3. In the presence of O_2, new radiation-oxidation reactions become possible. Thus $\mathrm{Cr}^{\mathrm{III}}$ and Cu^{I} are converted into $\mathrm{Cr}^{\mathrm{VI}}$ and $\mathrm{Cu}^{\mathrm{II}}$ with yields of 2 and 30 equiv/100 eV, respectively, while iodine formation in KJ solutions is observed from the very beginning of irradiation.

Fig. 3. Accumulation of I_2 as a function of time in a 0.01 M KJ solution irradiated in the absence of O_2. ↓ cessation of irradiation

Table 1 gives the yields of all the processes investigated. With the exception of $\mathrm{Cr}^{\mathrm{III}}$, J^-, and Cu^{I}, they refer to oxygen-free solutions.

The wide range of values of G leads to the conclusion that the reactions do not follow a single mechanism. They may be divided into two groups characterized by low and high yields and conditionally separated by a value of ~ 5 equiv/100 eV. It is noteworthy that all reduction reactions belong to the second group. Investigations carried out under various conditions (^{3,4}) make it possible to conclude that, when ionizing radiation acts on acetone, radicals $\dot{C}H_3$, $CH_3\dot{C}O$, $\dot{C}H_2COCH_3$, and H are formed with a total yield of 3-5 rad/100 eV. The EPR spectra of acetone irradiated at a temperature of -196°C, at which the radicals $\dot{C}H_3$ and H are not recorded, indicate an even lower yield, $G \sim 1.5$ rad/100 eV (^{2,5}). It follows from this that only reactions of the first group can be supplied during irradiation of solutions with the necessary amount of radicals. In oxygen-free solutions, oxidation of acceptors by radicals is most probable

CH_3CO. The absence of the oxidation product of the J^- ion, i.e., elemental iodine, during irradiation is explained by the high efficiency of its reaction with $\dot{C}H_3$ radicals $^{(6)}$, which also determines the disappearance of iodine upon irradiation of its solutions.

Table 1

Process	Eq/100 eV	Process	Eq/100 eV
1) $Fe^{II} \to Fe^{III}$	0.8	6) $Cr^{VI} \to Cr^{III}$	10.5
2) $Cr^{III} \to Cr^{VI}$ (O_2)	2.0	7) $Fe^{III} \to Fe^{II}$	14.5
3) $J \to J^-, RJ$	2.2	8) $Cu^{II} \to Cu^{I}$	17.3
4) $J^- \to J_2$ (O_2)	5.2	9) $Mn^{VII} \to Mn^{IV}$	20
5) $Cu^{I} \to Cu^{II}$ (O_2)	30	10) LMG → MG	25

In the presence of O_2 all the initial radicals $\dot{R}$ are converted into peroxide radicals $R\dot{O}_2$, which, like $CH_3\dot{C}O$, oxidize J^- ions; however, since the reaction $CH_3 + J$ is suppressed by the reaction $\dot{C}H_3 + O_2$, iodine appears already during irradiation. The determining role of a small number of primary radicals does not contradict the high yield of the oxidation reaction of Cu^{I} in the presence of O_2, since it should be regarded as coupled with a chain reaction of acetone oxidation initiated by primary radicals. The transition of Cu^{I} to Cu^{II} is effected through its interaction with the radical $R\dot{O}_2$ or with hydroperoxide ROOH.

Fig. 4. Dependence of $1/G$ (prod.) on 1/[acc.].
1–$Fe^{III} \to Fe^{II}$, 2–$Cu^{II} \to Cu^{I}$, 3–$Mn^{VII} \to Mn^{IV}$, 4–LMG → MG

In contrast to oxidation, the reactions of radiation reduction of ions of variable valence cannot be quantitatively accounted for by primary free radicals and require the use of other short-lived products of acetone radiolysis. Most probable is the participation of excited molecules, the number of which may in principle substantially exceed the number of ionization events. There is no direct information on the excited states of acetone subjected to ionizing radiation, but photochemical processes in its vapors have been well studied. Absorption of ultraviolet light, characterized by a long-wavelength limit of $\lambda \sim 3500$ Å ($h\nu \sim 3.5$ eV), causes fluorescence in the region 3800–4700 Å, consisting 90% of a component with $\tau = 2 \cdot 10^{-4}$ sec, attributed to the triplet state (7,8). This component is sharply quenched by oxygen and diacetyl, causing fluorescence or decomposition of the latter (9). Apparently, analogous excited states also arise under the action of electrons, since fluorescence with the same spectrum appears in irradiated frozen acetone (10). It may be assumed that excitation is capable of being transferred to the acceptor, causing its chemical transformation in a process competing with deactivation and energy transfer to solvent molecules.

The simplest kinetic scheme, taking into account the stationary concentrations of intermediate products, gives for the dependence of the product yield on

acceptor concentration, to the expression

$$\frac{1}{G(\text{prod})} = \frac{1}{G_0}\left(1 + \frac{A}{k[\text{acc}]}\right),$$

where G_0 is the yield of excited molecules; A includes the parameters of processes that do not involve the acceptor. As can be seen from Fig. 4, a linear dependence is satisfactorily obeyed in the case of reduction of Fe^{III}, Cu^{II}, Mn^{VII}, and oxidation of LMG. For G_0, a value of ~ 23 excited molecules/100 eV is obtained, and the ratio corresponding to the slopes of the straight lines,

$$k_{\text{Fe}^{\text{III}}} : k_{\text{Cu}^{\text{II}}} : k_{\text{Mn}^{\text{VII}}} : k_{\text{LMG}} = 2 : 2.5 : 3.5 : 10$$

reflects the order of activities of the acceptors. In the case of CrO_3, kinetic treatment leads to a substantially smaller value of G_0, which may be interpreted as the use of another radiolysis product for reduction.

Ions of variable valence form solvates with polar solvents with partial electron transfer, which is readily completed upon some excitation (^{11}). In the cases considered, acetone is the electron donor, and the energy transferred by the excited solvent molecules to the solvates makes reduction possible. This mechanism corresponds to that proposed by Kryukov and Dain (^{12}) for the photochemical reduction of FeCl_3 in aromatic hydrocarbons.

In the case of the radiation oxidation of LMG the mechanism is different, but the high yield of the process can likewise be associated with the transfer of excitation energy from acetone to the acceptor.

Institute of Electrochemistry
Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

Received
2 I 1963

REFERENCES

[1] V. A. Larin, N. A. Bakh, DAN, **139**, 703 (1961).
[2] V. A. Larin, A. D. Grishina, N. A. Bakh, DAN, **142**, 847 (1962).
[3] R. Ausloos, J. F. Paulson, J. Am. Chem. Soc., **80**, 5117 (1958).
[4] J. D. Strong, J. G. Burr, J. Am. Chem. Soc., **81**, 775 (1959).
[5] R. Smalier, M. S. Matheson, J. Chem. Phys., **30**, 695 (1959).
[6] G. R. Mastin, H. C. Sutton, Trans. Farad. Soc., **48**, 812 (1952).
[7] W. A. Noyes, E. B. Porter, J. E. Jolley, Chem. Rev., **56**, 49 (1956).
[8] J. Heicklen, W. A. Noyes, J. Am. Chem. Soc., **81**, 3858 (1959).
[9] J. Heicklen, J. Am. Chem. Soc., **81**, 3863 (1959).
[10] F. M. Hörl, J. Chem. Phys., **31**, 564 (1959).
[11] A. N. Terenin, Usp. Khim., **24**, 121 (1955).
[12] A. I. Kryukov, B. Ya. Dain, DAN, **138**, 153 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.