Isotope Exchange Reaction Between As(V) & As(III) in Acid Medium

H. J. ARNIKAR, V. G. DEDGAONKAR & (Miss) M. S. BARVE

Department of Chemistry, University of Poona, Poona 411007

As(III)/As(V) isotopic exchange reaction has been studied under different conditions by varying the concentration of the medium HCl from 2 to 10M and those of the reactants, As(V) and As(III), from 0·01 to 0·05M. The temperature is varied from 50° to 130°. Further, it has been shown that this isotopic exchange is possible also on irradiation with gammas. Following rate expression has been obtained:

$$R = k[As(V)]^{0·3}[As(III)]^0[HCl]^3$$

From the Arrhenius plot the activation energy for the exchange is found to be 67 kJ/mole.

WHILE studying the recoil chemistry of arsenic compounds following (n, γ) reactions we found that no isotope exchange occurred between arsenite and arsenate during dissolution of neutron irradiated sample in neutral or acidic medium[1,2]. However, there seems to be some evidence of slow exchange which becomes measurable after a much longer time. Maly and Simnova[3] had stated that the exchange is possible in boiling concentrated hydrochloric acid solution. Similarly, Anderson and Kahn[4] had reported a measurable exchange rate in HCl at concentrations around 10M even at lower temperatures (30-70°). The exchange curves were found to be complex for all temperatures which was attributed to the slow interconversion via hydrolytic reactions among several forms of As(V) which exchanged at different rates with As(III) present mostly as AsCl$_3$. Their spectrophotometric work revealed that the As(V) species existed in polymeric forms in HCl without attaining equilibrium even after several weeks. We undertook this work to find the dependence of the exchange rate on the concentration of the reactants and of the medium HCl and to determine the activation energy involved.

Materials and Methods

The ^{76}As tracer was obtained from the Bhabha Atomic Research Centre, Trombay, Bombay, in the form of HAsO$_2$ with a high specific activity of 750 mCi/g. As a part of the arsenic was in the As(V) state the whole of it was converted into As(V) state by oxidizing it with H$_2$O$_2$ in HCl medium.

The necessary reactant solutions using AR grade chemicals were prepared as follows:

Different concentrations of As(III) were obtained by dissolving appropriate amounts of pure As$_2$O$_3$ in HCl.

Some of the As(III) solute was oxidized by H$_2$O$_2$ and then diluted with HCl to necessary concentrations. This was then labelled with tracer ^{76}As in the As(V) state to the desired specific activity.

The reaction mixtures were prepared just before the experiment by mixing the stock solutions stored at room temperature. After flushing with nitrogen to remove dissolved oxygen, 2 ml of the reaction mixture were taken in 8 pyrex tubes and sealed under nitrogen atmosphere. These tubes were then placed for isothermal annealing in an electronically controlled oil-bath maintained at the desired temperature.

Separation of the two oxidation states of arsenic in the reaction mixture was carried out by the method followed by Wilson and Dickinson[5] in which As(V) was precipitated with magnesia mixture as MgNH$_4$AsO$_4$ while As(III) remained in solution. The As(V) precipitate was redissolved in 50% HCl and the activities in the arsenite and arsenate samples were determined using a liquid GM detector adopting the necessary corrections.

Results and Discussion

A part of the activity initially present wholly as As(V) was found in the As(III) sample following isothermal heating of the reaction mixture. The amount of activity in the As(III) state progressively increased with time of heating. Defining the fraction exchanged, F, as the ratio of the activity in the arsenite form at time t to that in equilibrium, the rate of exchange, R, was computed using the McKay[6] relation

$$\log (1-F) = -\frac{Rt[As(V)+As(III)]}{2·303[As(V)][As(III)]} \quad ...(1)$$

Finally the rate constant k was calculated using the relation

$$R = k[As(V)]^a[As(III)]^b[HCl]^c$$

where a, b, and c are constants giving the order of the exchange reaction with respect to As(V), As(III) and HCl concentrations respectively.

The log (1—F) versus t plots for all the parameters studied are linear; results for variation of temperature only are presented in Fig. 1 as an example. However, Anderson and Kahn[4], on the contrary, obtained curves which they could resolve into two linear portions. This difference might be due to the temperature of 100° used in the present work which is much higher than that used by Anderson and Kahn.
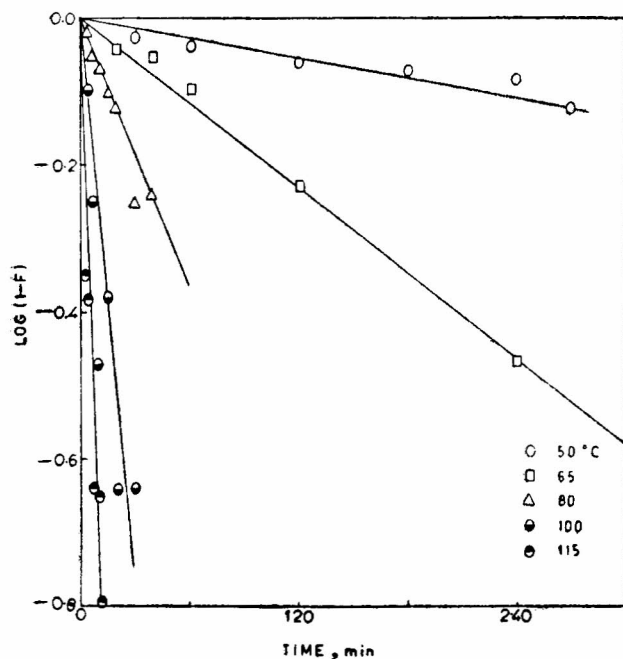
Fig. 1 — Variation of log $(1-F)$ versus time at different temperatures {[HCl] = $9.2M$; [As(III)] = [As(V)] = $0.025M$}
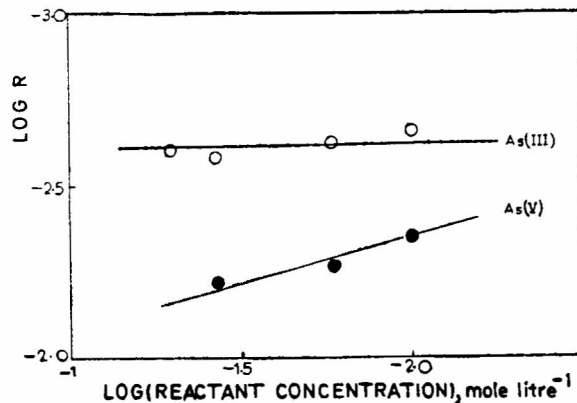

Fig. 2 — Variation of rate of exchange (R) with concentration of As(V) and As(III)

Fig. 3 — Variation of the rate of exchange (R) with HCl concentration

Effect of varying concentration of As(V) — Keeping other parameters constant, the concentration of As(V) was varied from 0.01 to $0.05M$. A linear relation is obtained when log R versus log [As(V)] is plotted, with a slope of 0.3 (Fig. 2). This fractional order supports the finding of Anderson and Kahn[4] that the exchange proceeds through a complex mechanism. These authors had shown that As(V) is present in various forms in HCl medium at room temperature as a result of slow inter-conversion, leading essentially to a complex process. However the linear variation of log $(1-F)$ with time observed presently at 80° shows that one form of As(V) only is taking part in the exchange, at least predominantly.

Effect of varying concentration of As(III) — The effect of varying [As(III)] on the exchange rate was studied by varying the concentration of As(III) in the range 0.01 to $0.05M$. The results are plotted in Fig. 2. The slope of the plot of log R versus log [As(III)] was zero, showing that the exchange rate is independent of [As(III)]. In HCl medium, most of As(III) ($> 98\%$) is present[7] as $AsCl_3$, which essentially must be taking part in the exchange process.

Effect of varying concentration of HCl — The HCl concentration was varied from 2 to $10M$, keeping other parameters constant. The exchange rate is highly dependent on the concentration of HCl increasing rapidly with the latter (Fig. 3).

Anderson and Kahn had shown by a spectrophotometric study of the As(V)-HCl system that the species of As(V) absorbing at 230 nm is highly susceptible to changes of HCl concentration[4]. The results plotted in Fig. 3 show that the exchange rate varies as the cube of [HCl] (Fig. 3). Cheek and coworkers[8] observed a similar trend in the Sb(III)-Sb(V) exchange. The observation of

Neuman[9] however, is contrary to these results. He finds, a decrease in the exchange rate with the increase in [HCl]. This remains unexplained.

Thus, on the basis of our results the overall rate expression can be written as

$$R = k[As(V)]^{0.3}[As(III)]^{0}[HCl]^{3}$$

k being the rate constant.

The rate of exchange is not affected by the cations Na^+ or Cd^{2+} added to the system.

Effect of varying temperature — The exchange reaction was studied at various temperatures, keeping the concentrations of the reactants constant. The log k versus $1/T$ plot (Fig. 4) was found to be linear, whose slope gave the energy of activation. For two independent series of experiments with 9.2 and $5.5M$ HCl, almost the same activation energy viz. 67 kJ/mole was obtained. Thus the same form of As(V) species appears to be responsible for the exchange at both the acid concentrations. This also shows that though the rate of exchange is mostly governed by [HCl], the mechanism of exchange is independent of the latter.
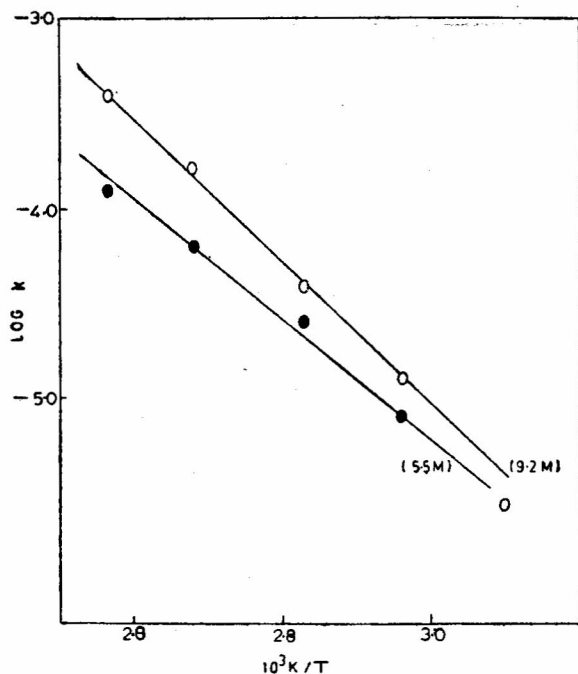
Fig. 4 — Arrhenius plot for the exchange reaction in 9·2 and 5·5M HCl

(pH 3). Thus the observed activity transfer in all probability is due to the isotopic exchange only induced by radiation. The log $(1-F)$ versus t plot was linear for doses up to 3 Mrad. The rate of exchange calculated from above data was found to be 4×10^{-4} mole litre^{-1} hr^{-1} at the dose rate of 0·08 Mrad/hr.

From the rate expression, it appears that HCl molecules must be involved in the rate determining step. Further, as the rate of exchange is almost independent of the concentration of As(III) in the form of $AsCl_3$, the reaction with As(III) should be a rapid one. The exact nature of As(V) species taking part in the exchange, however, is not clear. It is therefore not possible at this stage to suggest a suitable mechanism for this isotopic exchange.

Acknowledgement

References

1. ARNIKAR, H. J., DEDGAONKAR, V. G. & BARVE, M. S., Proc. Symp. Chemistry, Aligarh, 1972.
2. ARNIKAR, H. J., DEDGAONKAR, V. G. & BARVE, M. S., J. Univ. Poona, 44 (1973), 31.
3. MALY, J. & SIMANOVA, R., Chem. Listy, 49 (1955), 414.
4. ANDERSON, L. L. & KAHN, M., J. phys. Chem., 66 (1962), 886.
5. WILSON, J. N. & DICKINSON, R. G., J. Am. chem. Soc., 59 (1937), 1358.
6. MCKAY, H. A. C., Nature, 142 (1938), 997.
7. ARCAND, G. M., J. Am. chem. Soc., 79 (1957), 1865.
8. CHEEK, C. H., BONNER, N. A. & WAHL, A. C., J. Am. chem. Soc., 83 (1961), 80.
9. NEUMANN, H. M. & BROWN, H., J. Am. chem. Soc., 78 (1956), 1843.
10. MÜLLER, J. C., FERRADINI, C. & PUNCHEAULT, J., Radiochem. Radioanal. Lett., 10 (1972), 53.

Radiation-induced exchange—A measurable activity was found in the As(III) form when a mixture of equal concentrations of As(V) (labelled with ^{76}As) and As(III) (0·05M each) in 9·2M HCl was exposed to gammas from a kilocurie ^{60}Co source. Our preliminary experiments revealed that neither oxidation of As(III) nor reduction of As(V), in concentrated HCl medium, occurs up to 3 Mrad dose in contrast to Muller's[10] findings but in dilute acid solution