Catalysis of Ionic Reactions by Polyelectrolytes. III. Quenching of Uranyl Ion Fluorescence by Iron(II) Ions in Poly(vinylsulfonic acid) Solution[1]

Issam A. Taha and Herbert Morawetz*

Contribution from the Polymer Research Institute and the Department of Chemistry,
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201.
Received June 15, 1970

Abstract: Addition of poly(vinylsulfonate) (PVS) to uranyl solutions at pH 2 leads to a reduction of their fluorescence intensity probably due to self-quenching of the UO_2^{2+} concentrated in the vicinity of the polyanion. At pH 3, UO_2^{2+} binding to the polymer produces a greater reduction in fluorescence intensity and a change in the shape of the fluorescence spectrum similar to the change observed when the acidity of the medium is increased. Addition of ferrous ions to solutions containing uranyl and PVS leads first to rapid fluorescence quenching produced by concentration of ferrous and uranyl ions in the polymer domain. This is followed by a pronounced increase in fluorescence intensity as the Fe^{2+} ions displace uranyl ions from the polymer binding sites. Eventually, the fluorescence decreases again as a consequence of the quenching of free uranyl. This behavior proves that exchange of bound and free counterions is negligible over the lifetime of the excited uranyl ion.

In previous communications from this laboratory[2] and a similar study elsewhere,[3] it was shown that a reaction involving two doubly charged cations (*e.g.*, $Co(NH_3)_5Cl^{2+}$ and Hg^{2+} or Fe^{2+}) may be accelerated by many orders of magnitude in solutions containing small concentrations of chain molecules with a high density of anionic charges along the macromolecular chain. This effect is mainly a consequence of the very large concentration of the counterions in the polyion domain, although specific effects of the polymer domains on the activation process of a particular reaction are also significant.[2d,4]

It was of interest to broaden this investigation to a study of the effect of the polyion on the efficiency with which the fluorescence of one counterion is quenched by a second counterion. This type of study differs in two important respects from the study described in our earlier report. (1) One of the reagents, the excited uranyl ion, is very short-lived and its lifetime has been estimated as 1.5×10^{-6} sec.[5] As we shall show, the dependence of the fluorescence intensity on the concentration of the quenching ion in the presence of a polyelectrolyte should be *qualitatively* different, depending on whether the exchange of counterions in the polymer domain and outside it is rapid or slow compared to the lifetime of the fluorescing species. (2) Since the quenching of the fluorescence of a counterion by another one is accentuated in the polymer domain, the observed fluorescence intensity will be sensitive to the UO_2^{2+} *outside* these regions, while in the reaction rates studied previously, reagent ions outside the polymer domain could be considered to make a negligible contribution. It may then be concluded that the two types of studies should yield complementary information.

Experimental Section

Inorganic Reagents. Uranyl solutions were prepared from reagent grade uranyl acetate dihydrate (Fisher Scientific Co.) in triply distilled water. Uranyl analysis was carried out by igniting an aliquot of the solution at 900° for 20 min and weighing the resulting U_3O_8.

Fresh ferrous ion solutions (in 10^{-3} *M* perchloric acid) were prepared from analytical reagent grade ferrous perchlorate hexahydrate (G. Fredrick Smith Chemical Co.). The solutions were analyzed for Fe(II) by measuring the optical density of the *o*-phenanthroline complex at 512 nm[6] and for Fe(III) by measuring the optical density of the salicylate complex at 530 nm.[7] Less than 1% of the total iron was in the ferric state. Oxygen-free nitrogen was bubbled continuously through the solutions until used.

Polymer. The sodium salt of poly(vinylsulfonic acid) (PVS), prepared from the monomer (Columbia Organic Chemicals Co.) as described previously,[8] was obtained from Dr. G. Gordimer. The C/S ratio of the polymer was 0.746 (calcd 0.749). Solutions of PVS were made up gravimetrically.

Spectroscopy. Ultraviolet absorption spectra were determined in 1- and 10-cm cells using a Beckman DU-2 spectrophotometer.

Fluorescence measurements were made in a Hitachi MPF-2A spectrophotometer equipped with excitation and emission monochromators. The solutions were excited at 292 nm and the emission fluorescence was scanned between 460 and 600 nm. Slit openings corresponding to 8 and 10 nm were used for excitation and emission, respectively. Fluorescence quenching was studied following the relative fluorescence intensities at 512 nm. The fluorescence of uranyl solutions increased only about 8% upon bubbling deoxygenated N_2 through the solution for 10 min. This small quenching by oxygen was neglected and fluorescence determinations were made without deoxygenation.

Separate solutions were prepared to follow the dependence of fluorescence quenching on Fe^{2+} concentration. In making up these solutions, an aliquot of stock solution of PVS was added to a solution containing all the simple electrolytes.

Results and Discussion

Effect of Poly(vinylsulfonic acid) on the Absorption and Fluorescence of UO_2^{2+}. The species existing in uranyl ion solutions are known to depend on concen-

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* Address correspondence to this author.

(1) Financial support of this research by Research Grant No. GM-05811 of the National Institutes of Health is gratefully acknowledged.

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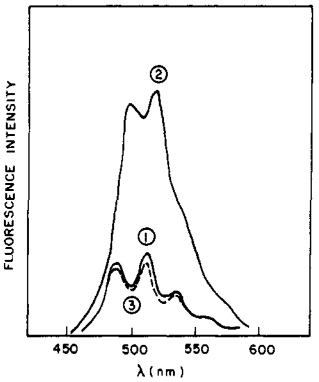

Figure 1. Fluorescence spectra of 5×10^{-4} M uranyl ion in solutions of (1) pH 2, (2) pH 3, (3) pH 3 in the presence of 3×10^{-3} N PVS.

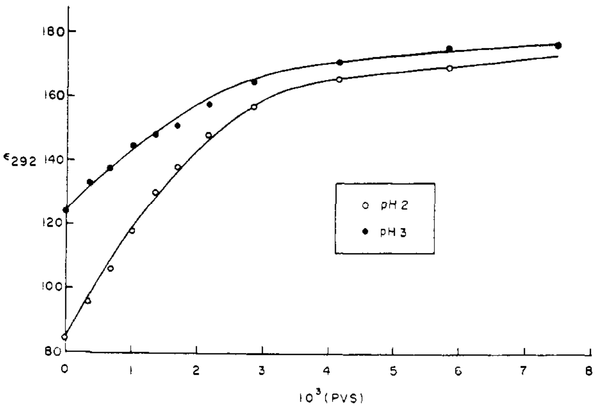

Figure 2. Effect of PVS on the absorption of 5×10^{-4} M uranyl ion.

tration and pH in a manner which may be represented by the equilibria

$$\begin{aligned}(U_2O_5^{2+})(H^+)^2/(UO_2^{2+})^2 &= K_1\\(U_3O_8^{2+})(H^+)^2/(U_2O_5^{2+})(UO_2^{2+}) &= K_2\end{aligned} \quad (1)$$

with still higher polynuclear species of the type $U_nO_{3n-1}^{2+}$ formed at higher pH values.[9-12] The careful analysis of titration data by Ahrland, *et al.*, yielded $\log K_1 = -6.05$, $\log K_2 = -6.35$. The change of chemical species with pH leads both to a change in the absorption spectrum of the uranyl solutions[9,10] and a change in the appearance of the fluorescence spectra.[13] Since part of the effect of the addition of a polyanion to a solution containing uranyl ions would be expected to be due to the accumulation of the uranyl in the polyion domain, in which hydrogen ions are also being concentrated, it was essential to obtain precise data on this acidity effect in order to interpret the effects observed in polyelectrolyte solution.

Figure 1 shows the fluorescence spectrum of 5×10^{-4} M uranyl solutions in the presence of 10^{-3} and 10^{-2} M $HClO_4$. The fluorescence spectrum in 0.01 M $HClO_4$ solution is characterized by relatively weak emission peaks at 488, 510, 535, and 560 nm. This spectrum may be taken as characteristic of the UO_2^{2+} ion as reported in the literature.[13,14] The form of eq 1 predicts that the relative concentration of UO_2^{2+}, $U_2O_5^{2+}$, etc., should be determined by the ratio $c/(H^+)^2$, where c is the stoichiometric uranyl concentration. This prediction was checked by the observation that solutions with $c = 5 \times 10^{-4}$, $(H^+) = 5 \times 10^{-4}$ and with $c = 13 \times 10^{-4}$, $(H^+) = 8 \times 10^{-4}$ had identical fluorescence spectra.

It should be noted that under our experimental conditions, *i.e.*, $c = 5 \times 10^{-4}$, $(H^+) = 10^{-3}$, Ahrland's equilibrium constants[12] would predict that only 0.05% of the uranyl would be in the form of $U_2O_5^{2+}$, while only 1 part in 10^7 would form the species $U_3O_8^{2+}$. The large change in the nature of the fluorescence spectrum observed under these conditions suggests, therefore, that the equilibrium constants for the condensation of UO_2^{2+} ions as formulated by eq 1 are substantially higher for the excited state of UO_2^{2+}. This would be analogous to the well-known shifts in pK values observed for many fluorescent acids or bases.[15]

The molar extinction coefficient of uranyl solutions with a stoichiometric concentration of 5×10^{-4} M at the excitation wavelength of 292 nm was found to be 81 in all solutions containing at least 0.002 M perchloric acid, and this extinction coefficient is presumably characteristic of the UO_2^{2+} ion. The value of ϵ_{292} increased with decreasing acidity of the medium, attaining values of 124, 334, and 704 in 10^{-3}, 5×10^{-4}, and 10^{-4} M perchloric acid solutions, respectively. Even at that lowest acid concentration, the values for K_1 and K_2 given by Ahrland[11,12] correspond to the conversion of only 4.5 and 0.11% of the 5×10^{-4} M uranyl ions to $U_2O_5^{2+}$ and $U_3O_8^{2+}$, respectively. The change in extinction coefficient $\Delta\epsilon$ from the limiting value observed in strongly acid solutions may then be considered to be proportional to the $U_2O_5^{2+}$ concentration.

Addition of poly(vinylsulfonate) (PVS) to uranyl solutions had no effect on the shape of the fluorescence spectrum in the presence of 10^{-2} M $HClO_4$. However, when the perchloric acid concentration was reduced to 10^{-3} M, the shape of the fluorescence spectrum changed with PVS addition in a manner similar to that observed on increasing the acidity of the medium. (See curve 3 in Figure 1.) The extinction coefficient at 292 nm increased with increasing PVS concentration in the presence of both 10^{-2} and 10^{-3} M $HClO_4$, but at high concentrations of the polyanion ϵ_{292} was almost the same at both pH values (Figure 2). It seems then that this change reflects both a shift in the equilibrium between UO_2^{2+} and $U_2O_5^{2+}$ and a change in the spectral properties of UO_2^{2+} when it is drawn into the polymer domain.

Let us now consider how the equilibria represented by eq 1 would be expected to be perturbed by the presence of a polyanion. If the electrostatic potential is ψ in the vicinity of the polyion, the singly charged hydrogen ion will be concentrated by a factor $\exp(e\psi/kT)$, where e is the electronic charge. Similarly, the doubly

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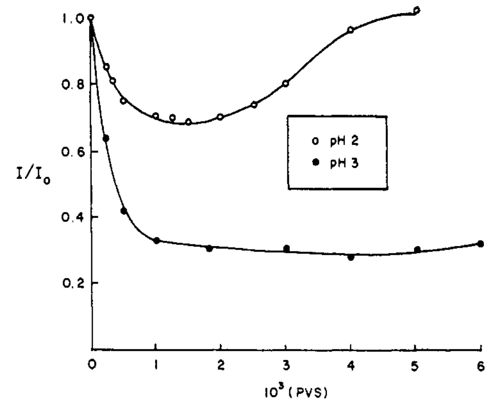

Figure 3. Effect of PVS on the fluorescence intensity of uranyl ion.

charged UO_2^{2+}, $U_2O_5^{2+}$, etc., will be concentrated by a factor $\exp(2e\psi/kT)$. Since eq 1 predicts, as stated above, that the $(U_2O_5^{2+})/(UO_2^{2+})$ ratio is determined by $c/(H^+)^2$, we must conclude that a simple model based on Coulombic forces does not predict any shift in the equilibrium governing the formation of polynuclear uranyl complexes in the presence of polyions.

This conclusion is obviously contrary to the evidence of the fluorescence spectra, but the discrepancy is hardly surprising if we consider the magnitude of the electrostatic interactions. This may be estimated from the fact that at low ionic strength and a high degree of neutralization, the apparent pK of poly(acrylic acid) increases by about three units,[16] which may be interpreted as a 1000-fold concentration of H^+ in the polyanion domain. A similar concentration of H^+ would be expected in the vicinity of PVS, which has the same spacing of ionized group along the chain molecule as the polyacrylate ion. However, it is clearly absurd to expect the uranyl ion to be concentrated by a factor of $(1000)^2$ leading, under our conditions, to a local concentration of 500 M.

It is instructive to consider the effect of PVS addition on the intensity of the fluorescence of the uranyl ion in the presence of 10^{-2} M $HClO_4$ since we need not consider, under these conditions, complications arising from the formation of polynuclear uranyl complexes. It may be seen in Figure 3 that on addition of PVS the fluorescence intensity decreases to a minimum but regains its original value in more concentrated PVS solutions. This phenomenon is similar to that observed by Bradley[17] in solutions containing acridine orange and deoxyribonucleic acid, and it may be considered to be the result of self-quenching of the UO_2^{2+} ions concentrated in the polymer domain.[18] The minimum in fluorescence intensity occurs at a PVS concentration somewhat higher than that corresponding to equivalence of the uranyl charges and the anionic sites of the polymer. In more concentrated PVS solutions, the local UO_2^{2+} concentration in the polyion domain is reduced, leading to an elimination of the self-quenching. Figure 3 shows also a plot of data obtained at pH 3. There the decrease in fluorescence intensity with increasing PVS concentration seems to arise mainly from the elimination of excited $U_2O_5^{2+}$, and the fluorescence does not increase again at high polymer concentrations.

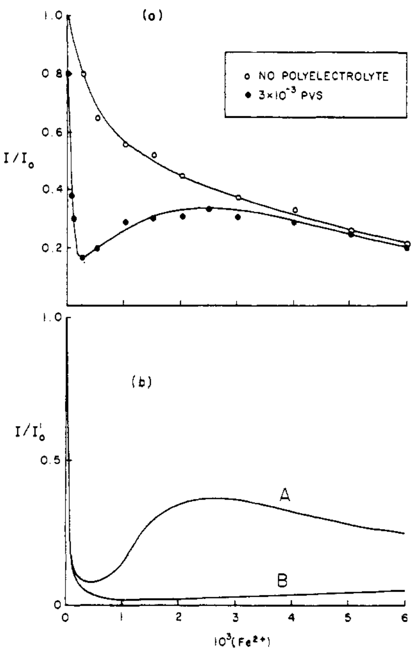

Figure 4. Effect of PVS on the fluorescence quenching of 5 × 10^{-4} M uranyl by Fe^{2+} in the presence of 10^{-2} M $HClO_4$: (a) experimental data, (b) calculated dependence of fluorescence quenching of 5 × 10^{-4} M uranyl in 3 × 10^{-3} N PVS assuming no counterion exchange (A) or infinitely fast counterion exchange (B). See the text for the parameters used in the calculation.

Quenching of Uranyl Ion Fluorescence by Fe^{2+} in the Absence and Presence of PVS. At pH 2 and in the absence of polymer, the quenching of the fluorescence of uranyl ion depends on the concentration of added Fe^{2+} as predicted by the Stern–Volmer relation[19]

$$I_0/I = 1 + k_{sv}(Fe^{2+}) \qquad (2)$$

where I_0 and I are the fluorescence intensities in the absence and the presence of the quenching agent and k_{sv} is the Stern–Volmer constant. The data plotted in Figure 4a correspond to k_{sv} = 585.[20,21] However, eq 2 has been derived on the assumption that the absorption of the exciting radiation by the quenching agent is negligible, and this assumption has to be justified for the present case. If the light has to traverse a distance x through the absorbing solution before exciting a fluorescing molecule, and if the emitted light has to pass a distance y before emerging from the fluorescence cell, the light intensity will be attenuated by a factor $\exp[-2.303(x + y)\Sigma E_i c_i]$, where E_i and c_i are the extinction coefficients and the concentrations of the species present in the solution. For a 1-cm square cell the attenuation factor q due to light absorption is then

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[21] The Stern–Volmer constant may be interpreted as the product of k_q, the second-order rate constant for the quenching process, and τ, the lifetime of the excited state. Using τ = 1.5 × 10^{-6} sec for UO_2^{2+},[4] we obtain the unusually high value of k_q = 4 × 10^8.

$$q = \int_0^1 \int_0^1 \exp[-2.303(x + y)\sum E_i c_i]\mathrm{d}x\mathrm{d}y \qquad (3)$$

$$q = [(1 - e^{-2.303\Sigma E_i c_i})/2.303\sum E_i c_i]$$

Using D and D_0 for $2.303\Sigma E_i c_i$ in the presence and in the absence of the quenching agent, we obtain a ratio $(I/I_0)_{\mathrm{abs}}$ due to absorption effects alone given by

$$(I/I_0)_{\mathrm{abs}} = \frac{D_0(1 - e^{-D})}{D(1 - e^{-D_0})} \qquad (4)$$

Let us apply this expression to a solution containing 5×10^4 M UO_2^{2+} and 10^{-3} M Fe^{2+}. The extinction coefficients of these two species at 292 nm are 81 and 11, respectively, yielding $D_0 = 0.092$ and $D = 0.117$. This leads to $(I/I_0)_{\mathrm{abs}} = 0.976$. The value of I/I_0 actually observed with 10^{-3} M Fe^{2+} was 0.63. We see then that absorption effects are, indeed, quite small compared to the quenching efficiency of Fe^{2+}.

The fluorescence intensity of uranyl ions in the presence of PVS, also shown in Figure 4a, depends in a much more complicated manner on the Fe^{2+} concentration. As long as the Fe^{2+} is very dilute, the quenching efficiency is increased by a large factor, since both the excited uranyl and the quenching ions are concentrated in the polymer domain. However, higher concentrations of ferrous ion lead to the displacement of the uranyl from the polyanion binding sites. This brings increasing concentrations of uranyl into regions where the ferrous ion concentration is much lower than in the vicinity of the polymer. It also eliminates the self-quenching of uranyl fluorescence resulting from the concentration of UO_2^{2+} in the polyion domains. These two factors explain the striking increase in the fluorescence which was observed as the Fe^{2+} concentration was raised from 2×10^{-4} to 2×10^{-3} M. At still higher ferrous ion concentrations, a slow decrease of fluorescence intensity was observed which may be interpreted as due to the quenching of uranyl ions outside the polymer domains. Light absorption, as discussed above, also becomes a significant contributing cause of decreased fluorescence at the highest Fe^{2+} concentrations employed (*e.g.*, with 6×10^{-3} M Fe^{2+}, $(I/I_0)_{\mathrm{abs}} = 0.87$).

Rate of Counterion Exchange. It can be shown that in a polyelectrolyte solution the fluorescence intensity of a counterion should depend in a *qualitatively* different manner on the concentration of a second counterion depending on the extent of exchange of bound and free counterions over the lifetime of the excited species. Let us consider the limiting cases of infinitely slow and infinitely fast exchange.

(a) Infinitely Slow Exchange. In this limiting case, the bound and free counterions make separate contributions to the fluorescence intensity, each of them being governed by the concentration of quenching ions in its vicinity. In our system, we assumed in first approximation that the doubly charged species UO_2^{2+} and Fe^{2+} had the same affinity for the polyion, and that counterion binding was governed by a simple equilibrium of the form

$$\frac{(M - B)(P/2 - B)}{B} = K \qquad (5)$$

where M is the stoichiometric concentration of divalent counterions, B is the concentration of bound divalent counterions, $P/2$ is the concentration of polymer binding sites, and K is a dissociation constant. The fluorescence of free uranyl ions is governed by the concentration of free ferrous ions as described by eq 2, with k_{sv} having the same value as in polymer-free solutions. For the polyanion-bound uranyl, the fluorescence is governed by the effective local concentration c_{eff} of ferrous ion in the polymer domain. In analogy with the treatment used previously for the interpretation of rates of ionic reactions in polyelectrolyte solution,[2c] we may set $c_{\mathrm{eff}} = c_{\mathrm{max}}\alpha_{\mathrm{Fe}}$, where c_{max} stands for the effective local concentration of divalent ions on a polyanion which is saturated with them and $\alpha_{\mathrm{Fe}} = 2(\mathrm{Fe})(B/M)/P$ represents the fraction of binding sites occupied by Fe^{2+}. On this basis we obtain

$$\frac{I}{I_0'} = \frac{f(1 - \alpha)}{1 + k_{\mathrm{sv}}(\mathrm{Fe}^{2+})(1 - \alpha)} + \frac{\alpha}{1 + k_{\mathrm{sv}}'c_{\mathrm{max}}\alpha_{\mathrm{Fe}}} \qquad (6)$$

Here, I_0' corresponds to the fluorescence intensity of uranyl fully bound to the polymer domain in the absence of quenching ions, f is a factor by which the fluorescence intensity increases on release from the polyion due to the elimination of self-quenching, $\alpha = B/M$, and k_{sv}' is the Stern–Volmer constant applicable to quenching in the polymer domain.

(b) Infinitely Fast Exchange. In this limit, the fluorescence quenching of an UO_2^{2+} ion will be governed by the average concentration of quenching ions present in its environment as it passes many times in and out of the polymer domain during the lifetime of the excited state. The result is

$$\frac{I}{I_0'} = \frac{\alpha + 1(1 - \alpha)}{1 + X} \qquad (7a)$$

$$X = (\mathrm{Fe}^{2+})[k_{\mathrm{sv}}(1 - \alpha)^2 + (2k_{\mathrm{sv}}'c_{\mathrm{max}}/P)\alpha^2] \qquad (7b)$$

The results obtained for the two limiting cases are qualitatively quite different. If there is no counterion exchange, even a small proportion of the fluorescing ions removed from the polymer domain to regions where the concentration of quenching ions is small will make a large contribution to the fluorescence intensity. On the other hand, the large value of c_{max}[2c] makes the second term on the right of eq 7b dominate the quenching in the limit of fast exchange, even if the fluorescing ion spends only a small fraction of its lifetime in the polyion domain.

The difference in the results obtained for the two limiting cases is illustrated in Figure 4b. Here we assumed $K = 2 \times 10^{-5}$, $f = 1.25$, $k_{\mathrm{sv}} = 6 \times 10^2$, and $k_{\mathrm{sv}}'c_{\mathrm{max}} = 10^2$. (The value of f corresponds to the ratio of fluorescence intensity observed in the absence of Fe^{2+}, in the absence of polymer, and in the presence of 3×10^{-3} N PVS, respectively. The value of $k_{\mathrm{sv}} = 6 \times 10^2$ approximates that observed at pH 2. The magnitudes of K and $k_{\mathrm{sv}}'c_{\mathrm{max}}$ were chosen so as to obtain a plot similar to that observed experimentally, although no claim is being made that a set of values could not be found to yield closer agreement with the experimental data. No allowance was made for light absorption by Fe^{2+}.) Curve A, representing slow counterion exchange, is quite similar to the results obtained (Figure 4a). The value of $k_{\mathrm{sv}}'c_{\mathrm{max}} = 10^2$ which best fits the experimental data is more than an order of magnitude lower than the value which would have been expected with $k_{sv}' = k_{sv}$ and with c_{max} similar to the values derived from previous studies of the catalysis of ionic reactions in PVS solutions.[2c,d] On the other hand, curve B is clearly qualitatively different from the experimental data. There can be no doubt that these data prove that no significant counterion exchange takes place over the short lifetime of the excited uranyl ion. While this may have been expected in view of previous estimates of counterion exchange rates,[22-24] the method employed in the present study to substantiate this conclusion should be of some interest, since it is applicable to exchange rates which are much too fast to be investigated by conventional techniques.

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Isotopic Exchange Reactions Involving Alcohols, Ketones, and Deuterium on Silica, on Palladium/Silica, and on Alumina

William R. Patterson and Robert L. Burwell, Jr.*

Contribution from the Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received April 18, 1970*

Abstract: The following two reactions, (I) $i\text{-}C_3H_7OD$ + butanone = $i\text{-}C_3H_7OH$ + butanone-*d* and (II) alcohol–ketone interchange, 2-propanol + butanone = acetone + 2-butanol, were catalyzed by a commercial silica at impurity centers, perhaps Al^{3+}. Reaction I is about 100 times as fast as (II) at 100–150°. Reaction II involves a rate-limiting hydride transfer as tested by use of 2-propanol-*2-d*. Reactions I and II are very much slower on pure silica. Both reactions occurred on a commercial palladium/silica catalyst at roughly the same rate as on commercial silica. The reactions must occur in part on the support, but palladium metal is also active for reactions I and II. In addition, isotopic exchange between deuterium and the hydroxyl hydrogen atoms of ethanol, 2-butanol, and *tert*-butyl alcohol on palladium/silica is about as rapid as reaction I. Isotopic exchange between butanone and deuterium is nearly as rapid. The rate of dehydrogenation of 2-butanol to butanone is only about 0.0001 that of formation of ROD. In addition, skeletal exchange of 2-butanol occurs on palladium/silica at a rate about 0.01 that of formation of ROD. Compared with platinum and nickel, palladium appears to have a low tendency to cleave the H–COH bond of secondary alcohols but a high tendency to cleave the HCO–H bond.

In recent years, alcohol–ketone interchange reactions have been reported to occur upon passage of the vapors of alcohol–ketone mixtures over various metal and metal oxide catalysts. For example, Malinowski and Kobyliński[1] observed the conversion of a mixture of isovaleraldehyde and ethyl alcohol to isoamyl alcohol and acetaldehyde on several metals supported on pumice. High conversions were obtained with nickel and with copper at 200–300°. 2-Propanol was a better hydrogen donor than ethanol which in turn was better than methanol. Similar interchange accompanied hydrogenation and dehydrogenation in 2-propanol–butanone mixtures passed over unsupported copper catalysts at 115–150°.[2] The reaction was also observed in preliminary experiments on a palladium/alumina catalyst at 96–130°.[2] We decided to extend the study of palladium catalysts because the low activity for hydrogenation of alkyl ketones on palladium permits one to observe reactions in the ketone–alcohol system which are hidden by hydrogenation on most group VIII metals. We started with palladium/silica catalysts because we feared that the interchange observed on palladium/alumina might have occurred on the support.

Initial work disclosed that both the interchange reaction and isotopic exchange between ROD and ketone occurred on commercial silica gel. Accordingly, these reactions were further investigated on palladium/silica, commercial silica gel, pure silica gel, and alumina. Silica gels and aluminas are widely used as supports for catalytically active metals and oxides. It has long been recognized that the catalytic characteristics of alumina can influence the total catalytic behavior of catalysts using alumina as a support. Silica gels, on the other hand, have usually been considered inert. For certain reactions, we will show that commercial silica gels have substantial catalytic activity but that pure silica gel is indeed inert or almost so.

Experimental Section

Materials. Ethanol, 2-propanol, 2-butanol, *tert*-butyl alcohol, and butanone were purified by fractional distillation and were chromatographically homogeneous. 2-Propanol-*O-d* was prepared by mixing isopropyl alcohol with deuterium oxide, salting out the alcohol, and distilling it. 2-Propanol-*2-d* of 98.5% isotopic purity (Volk Radiochemical Co.) was used without further purification.

The 0.3% palladium/silica catalyst (Baker and Co., Inc.) was crushed and sieved to 60–80 mesh. It was diluted with three to four times its weight of Pyrex beads of the same mesh size. Before used it was treated in a stream of hydrogen at 350° for about 10 hr. The following silicas were employed: (1) 60–200 mesh Davison Chemical Co., Grade 950 silica gel, washed with water and then dried; (2) Filtros FS-140-L (Filtros Incorporated, East Rochester, N. Y.), a low-area (~1 m^2/g), large-pore silica reported

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