Pulse Radiolysis of $Hg(CN)_2$ in Aqueous Solutions

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The reduction of $Hg(CN)_2$ in deaerated aqueous solutions was studied by the pulse radiolysis technique. $Hg(CN)_2$ reacts with the e_{aq} with $k(e_{aq}+Hg(CN)_2)=(1.3\pm0.1)\times10^{10}\ M^{-1}\ s^{-1}$ to yield a transient species of HgCN having an absorption maximum at 285 nm. $Hg(CN)_2$ is also reduced by CO_2^- with $k(CO_2^-+Hg(CN)_2)=(3.4\pm0.2)\times10^{9}\ M^{-1}\ s^{-1}$. The extinction coefficient of HgCN at 285 nm was determined as $(3.8\pm0.1)\times10^{3}\ M^{-1}\ cm^{-1}$. HgCN recombines with $2k=(3.4\pm0.5)\times10^{9}\ M^{-1}\ s^{-1}$ to produce another absorption species, assigned as $(HgCN)_2$, in an unstable state. The decay rate of the dimer was accelerated by some additives, such as alcohols and sodium formate. Making use of a proposed mechanism, $(HgCN)_2\rightarrow Hg(aq)+Hg(CN)_2$, the absorption coefficient of atomic mercury in water was evaluated as $(2.8\pm0.1)\times10^{3}\ M^{-1}\ cm^{-1}$.

The radiolysis of aqueous solutions of some metal ions gives various species in unstable valence states by the action of the reactive primary products coming from water, such as OH radicals, H radicals, and hydrated electrons. The technique of pulse radiolysis, as is well known, is useful in investigating the reaction processes of such short-lived species.¹⁾

By means of this method the radiolytic reduction of mercuric ions has, recently, been carried out in aqueous solutions.²⁻⁴⁾ The unstable monovalent mercurous ion formed initially behaves differently depending on pH of solutions. In an acidic solution at about pH 4,³⁾ the stable mercurous ion, Hg_2^{2+}, is formed *via* an additional step after disproportionation of the initial species:

$$Hg^+ + Hg^+ \longrightarrow Hg(0) + Hg(II)$$
$$Hg(0) + Hg(II) \longrightarrow Hg_2^{2+}$$

While in the neutral solution,⁴⁾ where the transient mercurous ion exists in the form of HgOH, the dimerization occurs in one step:

$$Hg^+ \longleftrightarrow HgOH$$
$$2HgOH \longrightarrow (HgOH)_2$$

The direct recombination is similar to the case of HgCl formed in the reduction of $HgCl_2$.⁵⁾

Another interesting point on radiolytic reduction of mercuric ion in the neutral solution was the finding of Hg_2O,⁴⁾ which had not been proved to exist before.

In comparison with these results, the pulse technique has been applied to aqueous $Hg(CN)_2$ solutions. Another transient mercurous species, HgCN, and its unstable dimer were found optically. The reaction mechanisms are discussed based on some kinetic data.

Experimental

The experimental details of pulse radiolysis measurement have been described previously.³,⁴⁾

Reagent grade $Hg(CN)_2$, HCO_2Na, methanol, ethanol, isopropyl alcohol and *tert*-butyl alcohol (all are supplied from Wako Pure Chemical Industries) were used without further purification.

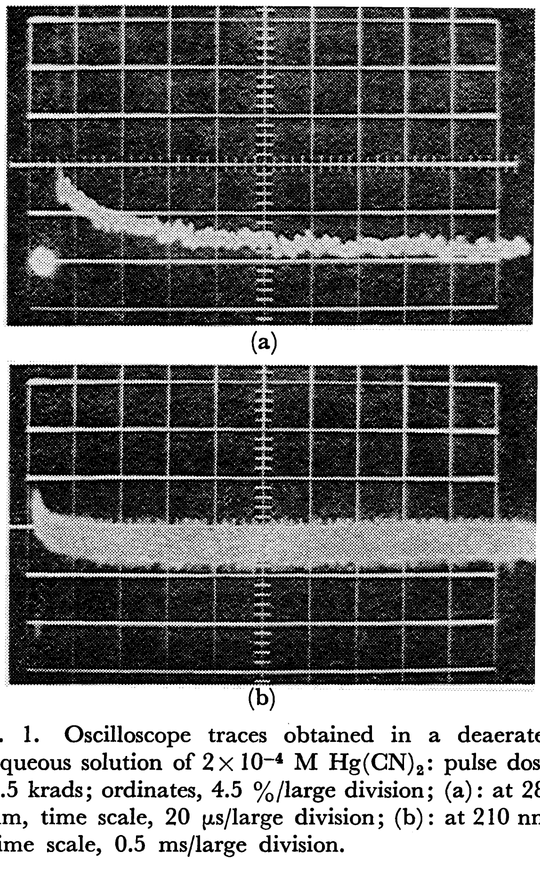
Triply distilled water was used at natural pH for all the experiments. All the solutions were deaerated by bubbling with argon. When necessary, solutions were saturated with N_2O (special pure grade, $O_2<0.1\%$, Suzuki Shokan Co.)

Product analysis in aqueous $Hg(CN_2)$ solutions containing isopropyl or *tert*-butyl alcohol was carried out on irradiation of 7.9 kCi ^{60}Co source at a dose rate of 1.29×10^5 r/hr. Acetone, being one of the products, was determined on a gas-chromatograph (Hitachi 063) using a column of 1 m Carbowax 20 M at 50 °C.

Results and Discussion

Figure 1 shows typical oscillograms of the changes in optical absorptions at 290 and 210 nm after pulse irradiation in a deaerated aqueous solution of 200 μM $Hg(CN)_2$. The absorption at 285 nm decays approximately according to a second order kinetics. The half life was about 30 μs for a dose of about 2.5 krads per pulse. While, the absorption at 210 nm decays only partly and thereafter remains constant within about 1 ms.

Figure 2 shows the spectra of the absorption immediately and 1 ms after the pulse. The initial spectrum has a peak at 285 nm and rises at wavelengths shorter


(a)

(b)

Fig. 1. Oscilloscope traces obtained in a deaerated aqueous solution of 2×10^{-4} M $Hg(CN)_2$: pulse dose, 2.5 krads; ordinates, 4.5 %/large division; (a): at 285 nm, time scale, 20 μs/large division; (b): at 210 nm, time scale, 0.5 ms/large division.

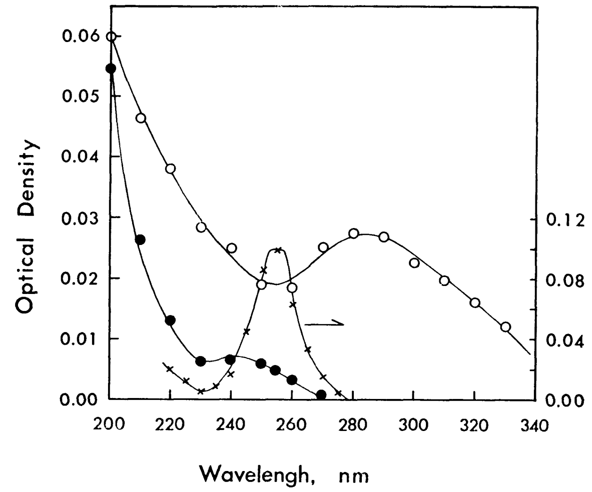


Fig. 2. Absorption spectra in a deaerated aqueous solution of 2×10^{-4} M $Hg(CN)_2$: average dose, 2.0 krads; immediately (○), 2 ms (●) after the pulse; (×), the spectrum about a few minutes after ten repeated pulses.

than 260 nm. The spectrum of the remaining absorption is different from that of the initial one. These absorption did not appear in solutions saturated with N_2O, but were hardly affected by the presence of 10 mM *tert*-butyl alcohol.

Absorption of the electron energy in water liberates the free radicals and molecular products represented by

$$H_2O \longrightarrow e_{aq}^-, H, OH, H_2, H_2O_2, etc. \quad (1)$$

It has been well known that N_2O and *tert*-butyl alcohol react rapidly with the e_{aq}^- and the OH radical, respectively:

$$e_{aq}^- + N_2O \longrightarrow N_2 + OH + OH^- \quad (2)$$

$$OH + t\text{-BuOH} \longrightarrow H_2O + t\text{-}\dot{B}uOH \quad (3)$$

where $k_2=5\times10^9\ M^{-1}\ s^{-1}$ [6] and $k_3=2.5\times10^8\ M^{-1}\ s^{-1}$.[7] Therefore, the scavenging effects suggest that the optical absorption appearing initially in aqueous solutions of $Hg(CN)_2$ could be due to the mercurous species, the reduced product of $Hg(CN)_2$ by the hydrated electron.

$$e_{aq}^- + Hg(CN)_2 \longrightarrow Hg(I) \quad (4)$$

The H radical would also function as a reducing agent for $Hg(CN)_2$, by analogy with the cases of other mercuric ions,[3,5,8,9]

$$H + Hg(CN)_2 \longrightarrow Hg(I) \quad (5)$$

though the contribution to the transient is small due to the low yield ($G_H/G_{aq^-}=0.2$).[10]

Reaction Kinetics of the e_{aq}^- and the CO_2^- Ion with $Hg(CN)_2$. In order to determine the rate constant of Reaction 4, the decay of the hydrated electron after the pulse of about 0.5 μs duration was monitored at 500 nm in the absence and presence of $Hg(CN)_2$. This monitoring wavelength is considerably longer than the absorption band of the transient product of Reaction 4. Under our experimental conditions, where 10 mM *tert*-butyl alcohol was present as a scavenger for the OH radical, the first half-life of the e_{aq}^- was roughly 15 μs. With increasing $Hg(CN)_2$ concentrations from 10^{-5} to 3×10^{-5} M the decay of the hydrated electron became first order and the half-life progressively diminished. As seen in Fig. 3, pseudo-first-order rate constants, calculated from these half-lives, were proportional to added substrate concentration over the range investigated. The second-order rate constant, obtained from data in Fig. 3, is $(1.3\pm0.1)\times10^{10}\ M^{-1}\ s^{-1}$. This is about half of the similar reaction to HgO[4] and about one third to $HgCl_2$.[5]

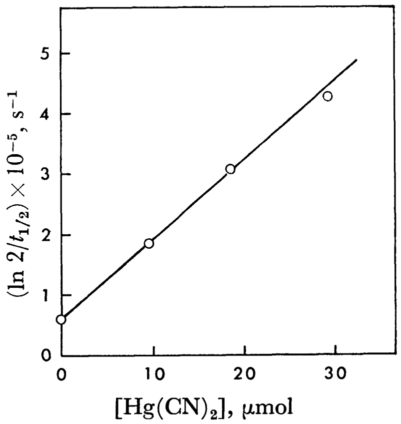


Fig. 3. Dependence of the pseudo-first-order decay rate of the e_{aq}^- on $Hg(CN)_2$ concentration, monitored at 500 nm.

On pulse radiolysis of a 200 μM $Hg(CN)_2$ solution containing 10 mM HCO_2Na and saturated with nitrous oxide, an analogous absorption species was also obtained by about 2 times in the absorption intensity, though the formation rate was slower. As a matter of fact, the spectrum immediately after the pulse was somewhat different from the spectrum in Fig. 2. In a short period of time after the pulse, however, the absorption built-up is observed in the wavelength region longer than 275 nm and shorter than 225 nm, while the absorption around 250 nm starts decaying at the end of the pulse. Within about ten μs the resultant spectrum of the absorption became analogous to the initial one in Fig. 2.

The HCO_2^- ion reacts with the OH or H radical to form a strong reducing species, CO_2^-, that has an optical absorption maximum at 250 nm:[12]

$$OH \text{ or } H + HCO_2^- \longrightarrow CO_2^- + H_2O \text{ or } H_2 \quad (6)$$

Thus it may be concluded that, similarly to the case of reduction by hydrated electron, the transient mercurous species results also from the reaction of $Hg(CN)_2$ with the CO_2^- radical ion:

$$CO_2^- + Hg(CN)_2 \longrightarrow CO_2 + Hg(I) \quad (7)$$

On analysis of the formation of the absorption at 285 nm, the plots of $\ln(D_\infty - D_t)$ *vs.* time, where D is the optical density, became linear and the slope was proportional to $Hg(CN)_2$ concentration. An example of the oscilloscope trace and kinetic plots are given in Fig. 4. In solutions of 50 and 100 μM $Hg(CN)_2$ a mean bimolecular rate constant for Reaction 7 was obtained as $(3.4\pm0.2)\times10^9\ M^{-1}\ s^{-1}$ at an average dose of 1.2 krads.

The experiments in the presence of some sorts of alcohols demonstrated that the transient mercurous species was not formed by the action of the radicals,

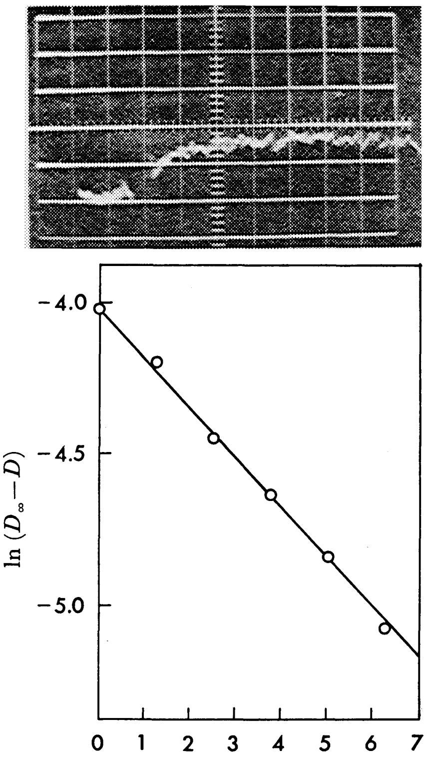


Fig. 4. An oscilloscope trace and first-order plots for the built-in of absorption at 285 nm in a N_2O saturated solution of 50 μM $Hg(CN)_2$ containing 10 mM HCO_2Na; dose, 1.2 krads; ordinates 4.5%/large division; time scale, 5 μs/large division.

such as $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, and $(CH_3)_2$-$C(OH)\dot{C}H_2$. These radicals were produced by the reactions of the corresponding alcohols with the OH radicals and have been known as reducing agents[13] except the last radical. Such results are different from the case where $HgCl_2$ is the reactant toward the alcoholic radicals. Nazhat and Asmus[5] have reported that $HgCl_2$ is reduced by the isopropyl alcohol radical to form a transient mercurous chloride, HgCl.

Characteristics of the Initial Transient Species. The optical density of the absorption immediately after the pulse at 285 nm was linear against dose up to about 3 krads/pulse in deaerated aqueous solutions of more than a few mM $Hg(CN)_2$ and HCO_2Na. The molar extinction coefficient of the species, ε^{285}, is $(3.8\pm0.1)\times 10^3\ M^{-1}\ cm^{-1}$, assuming $G_{Hg(I)} = G_{e^-_{aq}} + G_H + G_{OH} = 6.1$[10] in a 10 mM $Hg(CN)_2$ solution containing 5 mM HCO_2Na.

A possibility that might be argued on the assumption concerning the *G* value of the transient is the addition of H atoms or OH radicals to the $-C{\equiv}N$ bond and subsequent oxidation of the ligand. Such reactions possibly take place with rapid rates when H atoms or OH radicals react with HCN or free CN^-.[14] To confirm this possibility, pulse radiolysis of N_2O saturated aqueous solutions containing a concentration of benzene (200 μM) and several concentrations of $Hg(CN)_2$ was carried out. In such solutions most of initial reactive species are OH radicals that react with benzene to produce the hydroxycyclohexadienyl radical with an absorption maximum at 313 nm ($\varepsilon^{313} = 4.7\times 10^3\ M^{-1}\ cm^{-1}$).[15] No decrease in the absorption due to the radicals was observed with addition of $Hg(CN)_2$ up to 1 mM. Considering the competitive kinetics, the result demonstrates that the OH radical does not react with $Hg(CN)_2$ to a significant extent in these solutions. The nonreactivity of the $-C{\equiv}N$ bond seems to be similar to the case for the reaction of the H radical with the $Fe(CN)_6^{4-}$ ion,[16] though there is no data concerning the reactivity against the OH radical in Ref. 16.

Figure 5a shows the test of a second order rate law for the decay of the transient at 285 nm, for different doses, in a 1 mM $Hg(CN)_2$ and 5 mM HCO_2Na solution. In both cases in which the dose per pulse was 2.1 and 4.0 krads, respectively, the plots of $1/D$ *vs.* time are linear. Thus, the kinetics indicate the following reaction:

$$2Hg(I) \longrightarrow \text{product} \qquad (8)$$

and then the slope corresponds to $2k_8/\varepsilon l$, where ε is the extinction coefficient of the absorption and l the optical path length (1.5 cm here). All the slopes obtained for various combinations of $Hg(CN)_2$ concentration (0.2—10 mM) and HCO_2Na (1—100 mM) were in good agreement with a value of $2k_8/\varepsilon^{285}l = (5.9\pm0.4)\times 10^5\ s^{-1}$. The value was also not affected by the existence of $NaClO_4$ up to 100 mM in a solution containing the substrates in low concentration, as seen in Fig. 5a. Substituting the values of ε^{285} and l, $2k_8$ can be calculated as $(3.4\pm0.5)\times 10^9\ M^{-1}\ s^{-1}$.

According to the Debye-Hückel theory of reaction rates in solution, the lack of the effect of ionic strength on the rate suggests that the transient does not carry any charge on it and be assigned most likely to HgCN. It is concluded in addition that the species is not subject to

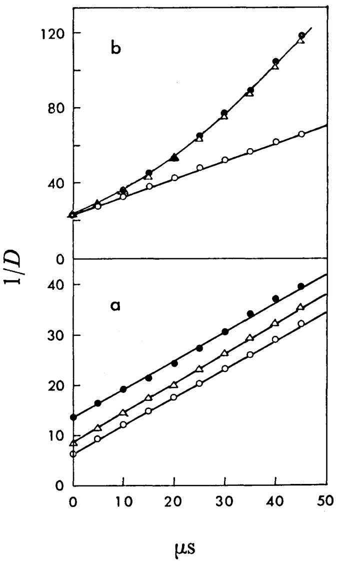


Fig. 5. Second-order plots for the decay of transient absorption at 285 nm, (a): $[Hg(CN)_2] = 1.0$ mM, $[HCO_2Na] = 5$ mM; ○: dose, 4.0 krads; ●: dose, 2.1 krads; △: 0.1 M $NaClO_4$ further contained, dose, 3.0 krads; (b): $[Hg(CN)_2] = 1.0$ mM, dose, 2.6 krads; ○: without additives; ●: 1 mM MeOH; △: 100 mM MeOH.

additional complexing with the HCO_2^- ion, since all the spectral observations and kinetic results were not influenced by addition of the ion. Figure 5b shows similar plots of the transient obtained in a solution containing methanol to scavenge the OH radical. In this case, the decay is no longer of simple second order. The shapes of the decay curves were not influenced at all by methanol concentration in the range from 1 to 100 mM. It might be concluded, therefore, that 1 mM of methanol is enough to scavenge all OH radical to form CH_2OH and that the increase in decay rate with the addition of methanol is due to the onset of the reaction:

$$\dot{C}H_2OH + HgCN \longrightarrow \text{products} \qquad (9)$$

If the assumption is right, the rate of decay of HgCN will be given by

$$-d[HgCN]/dt = k_9[\dot{C}H_2OH][HgCN] + 2k_8[HgCN]^2$$

An approximate estimate of k_9 can be obtained from a comparison of the initial decay rate with that in the presence of 5 mM HCO_2Na.[17] Let the initial decay rates of HgCN in the presence of the alcohol and HCO_2-Na be R_1 and R_2, respectively. Then from the data we find $R_1=2.01\ R_2$ and

$$R_1 - R_2 = k_9[\dot{C}H_2OH]_0[HgCN]_0$$

$$1.01 = k_9[\dot{C}H_2OH]_0/2k_8[HgCN]_0.$$

Since the H radical reacts slowly with methanol,[18] it should contribute to the formation of HgCN and the initial yield of $\dot{C}H_2OH$ should be equal to G_{OH}. Then using $[\dot{C}H_2OH]_0/[HgCN]_0=G_{OH}/G_{e_{aq}^-+H}=0.85$, k_9 can be calculated as $4.0\times10^9\ M^{-1}\ s^{-1}$. Similar treatments were also made for solutions of 1 mM $Hg(CN)_2$ containing 5 mM ethanol, isopropyl alcohol, and *tert*-butyl alcohol, wherein respective alcohol radicals must be taken into account. Here, the H radical may also be regarded to contribute to the formation of HgCN.[19] All the results are listed in Table 1, together with k(OH +HgCN) obtained in a solution without any OH scavenger. In Fig. 5b is also shown a result obtained in a 1 mM $Hg(CN)_2$ solution. The plots are found to be rather close to a linear one. It may be explained by the fact that the OH radical is consumed more rapidly by the combination reaction ($k(OH+OH)=8\times10^9\ M^{-1}s^{-1}$,)[20] than the similar reaction of the alcohol radicals.[21]

TABLE 1. REACTION RATE CONSTANTS OF HgCN WITH THE OH AND SOME ALCOHOL RADICALS, $[Hg(CN)_2]=1$ mM, [ROH]=5 mM

Additive	R_1/R_2	$k(\dot{R}OH+HgCN)$, $M^{-1}\ s^{-1}$
MeOH	2.01	4.0×10^9
EtOH	1.98	3.9×10^9
2-PrOH	1.59	2.4×10^9
t-BuOH	1.41	1.6×10^9
Nothing	1.77	3.1×10^9 a)

a) The value will represent the reaction rate constant of the OH radical with HgCN.

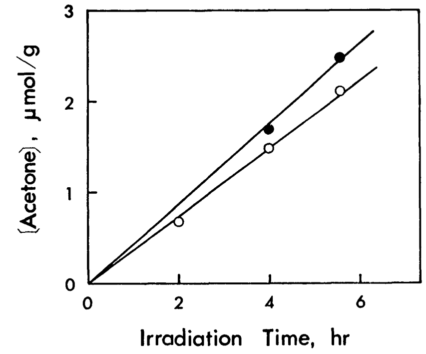


Fig. 6. Dependence of acetone yield on irradiation time in aqueous solutions of 10 mM isopropyl alcohol; ●: with saturated N_2O, ○: with 10 mM $Hg(CN)_2$; the radiation source: 7.9 kCi ^{60}Co, dose rate$=1.3\times10^5$ r/hr.

It is of interest whether Reaction 9′ gives a stable organomercury compound,

$$\dot{R}OH + HgCN \longrightarrow \text{products} \qquad (9')$$

where $\dot{R}OH$ means an alcohol radical. In order to obtain a few information about it, some experiments were performed in ^{60}CO γ-ray irradiation. Figure 6 shows the dependence of the amount of acetone produced on doses in an aqueous 25 mM isopropyl alcohol solution with 25 mM $Hg(CN)_2$ or with saturated N_2O. In each case the amount increases linearly with doses. From this data the G values of acetone were calculated as 3.0 ± 0.3 and 2.6 ± 0.3 in the solutions with $Hg(CN)_2$ and with N_2O, respectively.

In a N_2O saturated solution, all of the primary reactive species produced by irradiation of water are expected to contribute to hydrogen abstraction from isopropyl alcohol in the form of OH and H radicals,[18] since the e_{aq}^- is converted to the OH radical according to Reaction 2. The resultant radical, $(CH_3)_2\dot{C}OH$, would disproportionate to produce acetone with the G value of $1/2(G_{e_{aq}^-}+G_{OH}+G_H)=3.1$. The experimental result is in good agreement with this expectation. While, in the solution with $Hg(CN_2)$ the e_{aq}^- and the H radical contribute to the formation of HgCN. If Rection 9′ gives rise to a product, such as an organomercury compound that liberates no acetone molecule, the yield of acetone should be smaller than $1/2\cdot G_{OH}=1.4$. From this consideration our result of $G(\text{acetone})=2.6$ in this system demonstrates that most of the isopropyl radical reacts with HgCN to produce Hg(0) and acetone. The small decrease in the yield here may be explained by the contribution of Reaction 8. This conclusion is reasonable in view of the fact that the radical is a strong reducing agent.[13]

On the contrary the opposite conclusion seemed to be reached in the case of the *t*-BuOH radical that has not any reducing properties. Kelm *et al.* have proposed[22] that the radical is rapidly reduced to isobutene by the unstable Ni^+ ion on the radiolysis of an aqueous solution of $NiSO_4$ containing *t*-BuOH. However, no sign of isobutene formation was obtained gas-chromatographically on ^{60}CO γ-ray irradiation of an aqueous solution of $Hg(CN)_2$ with *t*-BuOH. Thus, the experimental result might present indirect evidence for the formation of an organomercury compound, such as $(CH_3)_2$-$C(OH)CH_2HgCN$.

Long-lived Species. In general, attempts to produce $Hg_2(CN)_2$ lead only to $Hg(CN)_2$ and mercury, although it has been suggested that it might be formed in non-aqueous solvents at low temperatures.[23] The unstability of $Hg_2(CN)_2$ has been explained by the reason that the CN^- ion forms a stable complex, $Hg(CN)_2$, with Hg^{2+} through the equilibrium, $Hg_2^{2+} \longleftrightarrow Hg + Hg^{2+}$ ($K = 1.15 \times 10^{-2}$). As seen in the case of Hg_2O,[4] however, a dimer complex of mercurous cyanide is also expected to be found in an unstable state. Thus, the residual absorption species in Fig. 2 may be assigned to a dimerized product, maybe as $(HgCN)_2$. As has been mentioned earlier, the second order reaction kinetics also supports this assignment, thus:

$$2HgCN \longrightarrow (HgCN)_2 \qquad (8')$$

A similar spectrum was obtained also with the doubled yield of absorption in solutions containing the HCO_2^- ion up to 100 mM. The dimerization of the initial species is expected to be fully attained in this solution, where there should be no reactant consuming the initial transient. Considering the stoichiometry in Reaction 8′, the absorption coefficient of the dimer was evaluated as $(5.2 \pm 0.2) \times 10^3$ M^{-1} cm^{-1} at 220 nm and $(1.1 \pm 0.05) \times 10^4$ M^{-1} cm^{-1} at 210 nm, from the slope of the yields against pulse doses in a solution of 3 mM $Hg(CN)_2$ and 5 mM HCO_2Na.

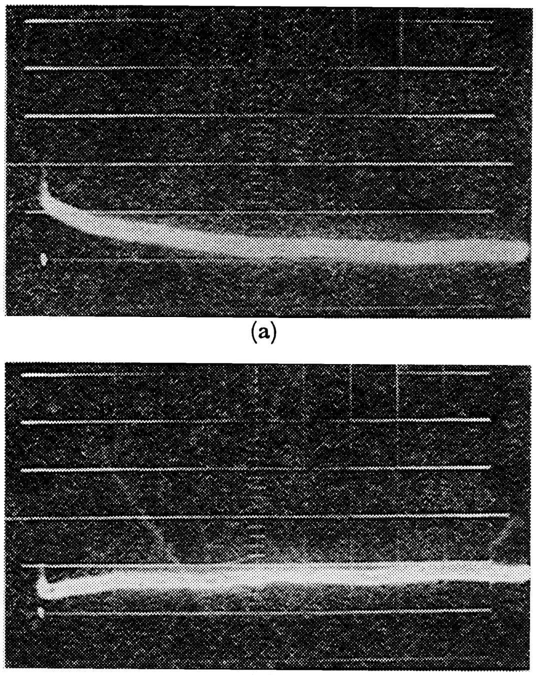
In solutions with alcohols, however, the absorption was somewhat larger at shorter wavelengths, which may indicate the contribution from the products arising from Reaction 9 or 9′.

As expected, the long-lived absorption observed at 210 nm was found to decay slowly in the solution without any additives. The decay kinetics did not follow either a first or a second order rate law. The initial half-life is (4±1) s independently of $Hg(CN)_2$ concentration in the range from 0.1 to 10 mM. Since the lifetime was not affected by the presence of 100 mM H_2O_2 added before irradiation, the decay was not due to the reaction with H_2O_2 produced by pulse electron irradiation. In solutions with additives, however, the decay rates become faster. The rates seemed to become constant at more than 5 mM of respective additives, although they were considerably scattered in every solutions. The most plausible half-lives obtained in each solution are listed in Table 2.

TABLE 2. MOST PLAUSIBLE HALF-LIVES OF $(HgCN)_2$ IN 1 mM $Hg(CN)_2$ SOLUTIONS WITH SOME ADDITIVES

Additive	mM	$[Hg(CN)_2]$ mM	λ_{obsd} nm	$t_{1/2}$ s
no		0.2—1.0	210	4 ± 1
			220	5 ± 1
MeOH	5—100	1.0	220	7×10^{-1}
EtOH	10	1.0	220	1×10^{-1}
2-PrOH	10	1.0	220	8×10^{-2}
t-BuOH	5	1.0	210	2.5×10^{-1}
HCO_2Na	5—10	1.0	220	10×10^{-3}

Figure 2 also shows an absorption spectrum about one minute after ten repeated pulses. The spectrum is very similar to that of atomic mercury dissolved in water.[24] Considering the low solubility of mercury[25] and the short optical path length of the analytical light, however, the absorption in its stable state is expected to be far lower. Thus, it is concluded that mercury dissolved temporarily in excess is produced following the decomposition of $(HgCN)_2$.


(a)

(b)

Fig. 7. Decay of the long-lived species at 220 nm (2.6 krads): (a); and increase of absorption at 254 nm (3.2 krads): (b); observed in a 1 mM $Hg(CN)_2$ solution containing 5 mM HCO_2Na; ordinates: 11%/large division, time scale: 5 ms/large division.

$$(HgCN)_2 \longrightarrow Hg(0) + Hg(CN)_2 \qquad (10)$$

A similar behavior has been found in the decomposition of Hg_2O produced by pulse electron irradiation in the neutral solution of mercuric oxide.[4] This conclution is further confirmed by the comparison of absorption changes with time between 254 and 220 nm. Figure 7 shows an example of a couple of oscilloscopic traces at the respective wavelengths obtained in a solution of 1 mM $Hg(CN)_2$ and 5 mM HCO_2Na. Simultaneous changes in absorption are found between the decay of the long-lived species at 220 nm and the formation of the additional absorption at 254 nm. The presence of alcohols as additives also gave similar results. These observations reasonably indicate that the species, the absorption of which increases slowly at 254 nm, has a dimerized mercurous cyanide molecule as its precursor. In solution without any additives, however, such increase in absorption at 254 nm was uncertain, maybe, due to a slow precipitation process of the dissolved mercury.

$$Hg(aq) \longrightarrow Hg(liquid) \qquad (11)$$

Since the decay of the dimer is more rapid in a solution containing HCO_2Na, Process 11 would be negligible at the time when the absorption just become constant in Fig. 7. Thus, if it is assumed that all the absorption at 254 nm, 50 ms after the pulse, is due to the dissolved mercury arising from Reaction 10, the extinction coefficient can be evaluated. Considering that the concentration of Hg(aq) is equal to that of its precursor, $(HgCN)_2$, ε^{254} of Hg(aq) is calculated as $(2.8 \pm 0.1) \times 10^3\ M^{-1}\ cm^{-1}$ from Fig. 7.

The kinetic behavior of the dimerized species in the presence of these additives seems to be similar to that in a neutral solution of unstable mercurous oxide, $(HgOH)_2$.[4] It is, however, still in question how the decay process is controlled.

References

1) G. E. Adams, J. H. Baxendale, and J. W. Boag, *Proc. Chem. Soc.*, **1963**, 241; D. Meyerstein and W. A. Mulac, *J. Phys. Chem.*, **72**, 784 (1968); A. S. Ghosh-Mazumdar and E. J. Hart, *Adv. Chem. Ser.*, **81**, 193 (1968); *etc.*

2) M. Faraggi and A. Amozig, *Int. J. Radiat. Phys. Chem.*, **4**, 353 (1972).

3) S. Fujita, H. Horii, and S. Taniguchi, *J. Phys. Chem.*, **77**, 2868 (1973).

3) S. Fujita, H. Horii, T. Mori, and S. Taniguchi, *ibid.*, **79**, 960 (1975).

5) N. B. Nazhat and K.-D. Asmus, *ibid.*, **77**, 614 (1973).

6) J. H. Baxendale *et al.*, *Nature* (London), **201**, 468 (1964).

7) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).

8) M. Faraggi and J. Désalos, *Int. J. Radiat. Phys. Chem.*, **1**, 335 (1969).

9) E. Hayon and M. M. Moreau, *J. Chim. Phys.*, **62**, 391 (1965).

10) *G* represents the number of species per 100 eV absorbed energy. Primary reactive species in Reaction 1 are produced with $G(e_{aq}^-)=2.7$, $G(OH)=2.8$, and $G(H)=0.6$, respectively.[11]

11) M. S. Matheson and L. M. Dorfman, "Pulsed Radiolysis," The M. I. T. Press, Cambridge, Mass. (1969).

12) J. P. Keene, Y. Raef, and A. J. Swallow, "Pulse Radiolysis," ed. by M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London (1965), p. 99.

13) J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **75**, 458 (1971); J. Lilie, *J. Phys. Chem.*, **76**, 1487 (1972).

14) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967); D. Behar, *J. Phys. Chem.*, **78**, 2660 (1974).

15) A. Mantaka, D. G. Marketos, and G. Stein, *ibid.*, **75**, 3886 (1971).

16) D. Zehavi and J. Rabani, *ibid.*, **78**, 1368 (1974).

17) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael, "Pulse Radiolysis," ed. by M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London (1965), p. 117.

18) J. Rabani, *J. Phys. Chem.*, **66**, 361 (1962).

19) (a) A. Appleby, G. Scholes, and M. Simic, *J. Amer. Chem. Soc.*, **85**, 3891 (1963); (b) J. Rabani, *J. Phys. Chem.*, **66**, 361 (1962); *J. Chem. Phys.*, **37**, 1865 (1962).

20) M. S. Matheson, *Radiat. Res. Suppl.*, **4**, 1 (1964).

21) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969).

22) M. Kelm, J. Lilie, A. Henglein, and E. Janata, *ibid.*, **78**, 882 (1974).

23) B. J. Aylet, "Comprehensive Inorganic Chemistry," Vol. 3, ed. by J. C. Bailar, H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, Perganon Press, Oxford (1973), p. 291

24) H. Reichardt and K. F. Bonhoeffer, *Z. Elektrochem.*, **36**, 753 (1930); *Z. Phys.*, **67**, 780 (1931).

25) S. S. Choi and D. G. Tuchk, *J. Chem. Soc.*, **1962**, 4080, A. Stock, *Z. Anorg. Allg. Chem.*, **217**, 241 (1934).