The Absorption Spectrum of the Cobalt(II) Ion Catalyst in the Reaction of Methanol with Carbon Monoxide and Hydrogen under a High Pressure

By Tsutomu MIZOROKI and Mikitake NAKAYAMA

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The treatment of methanol with carbon monoxide or carbon monoxide - hydrogen mixtures under a high temperature and pressure results in the formation of acetic acid, acetaldehyde and ethanol, as in the following equations:

$$CH_3OH + CO = CH_3COOH + 33.0^{*1} \quad (1)$$

$$CH_3OH + CO + H_2 = CH_3CHO + H_2O + 24.6 \quad (2)$$

$$CH_3OH + CO + 2H_2 = C_2H_5OH + H_2O + 51.2 \quad (3)$$

In the acetic acid synthesis from methanol and carbon monoxide represented by Eq. 1, mixtures of the salts of transition metals (nickel, iron, cobalt etc.) and iodine or the iodides of these metals have been used as the catalyst,[1,2] and a mixture of cobalt(II) acetate and iodine had been reported as a catalyst of the homologation of methanol[3], as is represented by Eqs. 2 and 3. On the other hand, no works have been reported on reaction mechanisms with these catalysts, because the complex intermediates from these catalysts are too unstable to be isolated at room temperature and pressure.

The present authors investigated in detail these reaction, in the presence of a mixture of cobalt(II) acetate ($Co(AcO)_2 \cdot 4H_2O$*2) and with an iodide (lithium iodide, sodium iodide, potassium iodide, etc.) as the catalyst, by using an autoclave lined with Ti-Mn alloy. It was reported that the conversion of methanol into acetic acid or acetaldehyde increased with the amount of an iodide added and that ethanol was estimated to be formed from the hydrogenation of the acetaldehyde produced.[4,5] On the other hand, it is well known that the soluble salts of cobalt(II) ions form blue or green tetrahedral complex ions $[CoX_4]^{2-}$ ($X=Cl^-$, Br^-, I^-, AcO^-, NCS^-, etc.[6]) in organic solvents (glacial acetic acid, acetone, nitromethane, etc.). From these facts, it was assumed that, during the course of the reaction, most of cobalt(II) ions were surrounded with iodide ions, thus forming tetrahedral complex ions of the $[Co(AcO)_{4-n}I_n]^{2-}$ type ($n=1$—4), with which carbon monoxide was then activated.[7]

This work was undertaken in order to study the behavior of cobalt(II) ions and iodide ions in the course of the reaction of methanol with carbon monoxide and hydrogen by measuring the absorption spectra. For this purpose, a special autoclave, with which absorption spectra could be observed under a high temperature and pressure, was made of Ti-Mn alloy and a couple of thick pieces of quartz glass.

Experimental

The Apparatus for Taking an Electronic Absorption Spectrum under a High Temperature and Pressure.—The special autoclave is illustrated in Fig. 1. A couple of thick quartz glass windows (15 mm. thick, 20 mm. in diameter) were set in teflon packings and pressed uniformly hard against the autoclave by high internal pressure introduced through a valve (1 in Fig. 1). These pieces of glass were proof against pressure lower than 250 kg./cm² at a temperature of 200°C. The inner volume of this autoclave was about 6 ml., and the thickness of a liquid sample was about 5.5 mm. The autoclave was heated by the electric furnace shown in Fig. 1. The temperature of the autoclave was kept constant (within ±0.5°C) by using an electronic thermo-controller (P. I. D. method), because the absorption spectrum of cobalt(II) ion was very dependent on the temperature. The autoclave was then placed with the electric furnace into the sample box of an automatic recording spectrophotometer (IV-50A type, Shimadzu Seisakusho Ltd.), and absorption spectra were recorded over the range from 340 to 1000 mμ.

The Reaction Conditions.—The reaction rate of the acetic acid synthesis by Eq. 1 was very slow at 200°C under pressure lower than 250 kg./cm². However, the reaction of the acetaldehyde synthesis

*1 $-\Delta H°$ (25°C) (kcal./mol.) obtained from the heats of combustion.

1) W. Reppe, *Ann. Chem.*, **582**, 72—83 (1953).

2) S. K. Bhattacharyya and S. Sourirajan, *J. Appl. Chem.*, **6**, 442 (1956); **9**, 126 (1959).

3) J. Berty and L. Marko, *Chem. Tech. (Berlin)*, **8**, 260 (1956).

*2 AcO=CH_3COO

4) T. Mizoroki, et al., *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **65**, 1049, 1054 (1962).

5) T. Mizoroki and M. Nakayama, This Bulletin, **37**, 236 (1964).

6) As for the literature, see Table I.

7) T. Mizoroki and M. Nakayama, *Catalyst (Shokubai)*, **5**, 203 (1963).

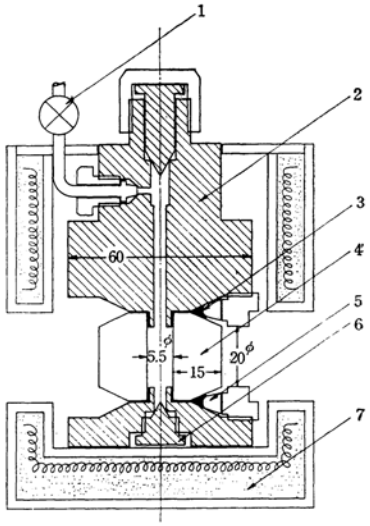

Fig. 1. A special autoclave with a couple of high pressure sight gasses.

1 A valve
2 Ti-Mn alloy
3 Teflon packing
4 Sight glass (Quartz)
5 Ti metal packing
6 Inlet of a liquid sample
7 Electric furnace

by Eq. 2 proceeded smoothly under the endurable condititons of the special autoclave, even if the amount of cobalt(II) acetate added was less than 0.10 mol. %. A preliminary experiment showed that the lowest partial pressures of carbon monoxide and hydrogen reacting with methanol to form acetaldehyde were, respectively, 70 and 30 kg./cm² at 200°C. From these experimental results, it was found that the following conditions were suitable for investigating the variation in the absorption spectrum of the cobalt(II) ion catalyst. The solution used was a mixture of methanol 9 and acetic acid*3 1 (mole ratio) containing 0.05 mol. % of cobal(II) acetate and a given amount of sodium iodide. After the solution of 3.0 ml. had been charged into the autoclave through inlet 6 in Fig. 1, carbon monoxide and hydrogen were introduced, up to 70 and 30 kg./cm² respectively (the total pressure, 100 kg./cm²). The autoclave was then heated up to 180—190°C within one hour. The methanol, acetic acid, cobalt(II) acetate and sodium iodide used were obtained from commercial sources, while the hydrogen and carbon monoxide were obtained from the electrolysis of water and the decomposion of formic acid respectively.

No attempt was made to evaluate the base line of a high temperature and pressure spectrum. Only the positions of the bands and the relative magnitude of the intensities of the recorded absorption spectra are important, since the transmittances, I/I_0 $(=T)$, were determined at 840 mμ, at which point that of the liquid sample was nearly constant. The formation of acetaldehyde was confirmed by subjecting the liquid sample, after an experiment had been finished to gas chromatography.

*3 Acetic acid was added to prevent the catalyst from precipitating.

Results and Discussion

Visible Absorption Spectra.—The variation in the absorption spectra due to the d-d transitions of cobalt(II) ions in the course of the reaction is recorded in Fig. 2. The amounts of the iodide ions of I, II, and III added in Fig. 2 are, respectively, 5, 10 and 20 times that of the cobalt(II) ion. IV shows a variation in the absorption spectrum of the cobalt(II) ion ($I^-/Co^{2+}=10$) in ethanol, with which carbon monoxide and hydrogen do not react under these conditions. V shows an absorption spectra of $[CoI_4]^{2-}$ and $[Co(AcO)_4]^{2-}$ in glacial

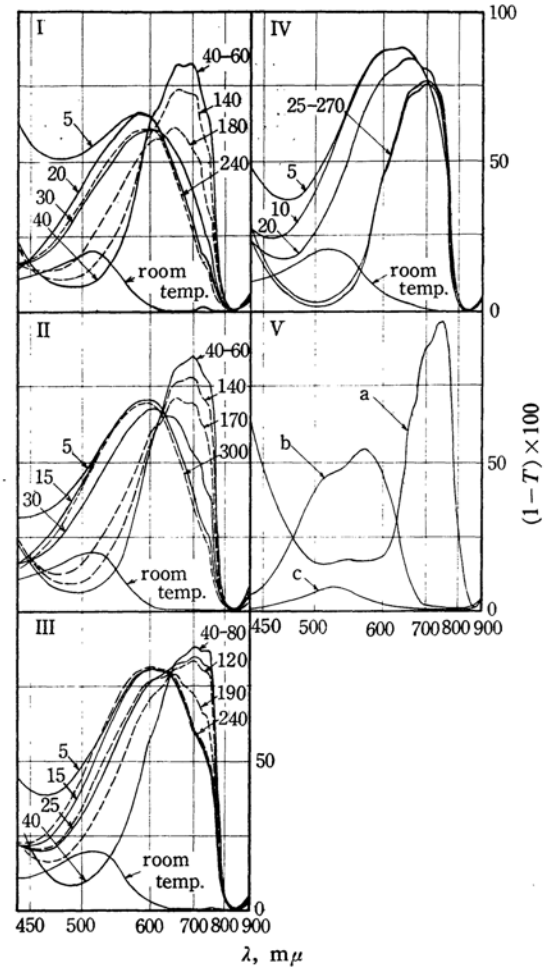

Fig. 2. The variation in the absorption spectra of cobalt(II) ions ($Co(AcO)_2 \cdot 4H_2O$ of 0.050 mol. %) in course of the reaction.

Numbers in the figure are the times (min.) after the temperature of the autoclave having reached 180°C. (I) $I^-/Co^{2+}=5$, (II) $I^-/Co^{2+}=10$, (III) $I^-/Co^{2+}=20$, (IV) $I^-/Co^{2+}=10$ in ethanol 9: acetic acid 1 sol. and (V) the absorption spectra of $[CoI_4]^{2-}$ (a), $[Co(AcO)_4]^{2-}$ (b) and $[Co(H_2O)_6]^{2+}$ (c).

TABLE I. THE ABSORPTION SPECTRA OF TETRAHEDRAL COBALT(II) COMPLEX IONS

Complex ion	Absorption range, mμ	λ, mμ (ε=max.)	ε ($mol^{-1}\,cm^{-1}$)	Solvent
$[Co(H_2O)_6]^{2+}$	450—550	530	17	H_2O
$[CoCl_4]^{2-}$ a)	500—730	693	653	CH_3NO_2
$[CoBr_4]^{2-}$ a)	520—750	698	790	CH_3NO_2
$[CoI_4]^{2-}$ a)	600—800	733	1126	CH_3NO_2
$[CoCl_4]^{2-}$ b)	560—720	697	612	CH_3COCH_3
$[CoBr_4]^{2-}$ b)	620—750	723	1090	CH_3COCH_3
$[CoI_4]^{2-}$ b)	650—830	777	1120	CH_3COCH_3
$[CoCl_4]^{2-}$ c)	550—720	685	650	AcOH
$[CoBr_4]^{2-}$ c)	600—750	695	900	AcOH
$[CoI_4]^{2-}$ e)	620—810	755	1050	AcOH
$[Co(AcO)_4]^{2-}$ d)	450—650	565	1700	AcOH
$[Co(CNS)_4]^{2-}$ c)	550—670	620	2500	AcOH

a) N. S. Gill, R. S. Nyholm, *J. Chem. Soc.*, **1959**, 3977.
b) D. A. Fine, *J. Am. Chem. Soc.*, **84**, 1139 (1962).
c) P. J. Proll, L. H. Sutcliffe, *J. Phy. Chem.*, **65**, 1993 (1961).
d) P. J. Proll, L. H. Sutcliffe, J. Walkley, ibid, **65**, 455 (1961).
e) T. Mizoroki, Y. Andō, S. Furumi, The 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.

acetic acid: (a) is that of $[CoI_4]^{2-}$ formed at a room temperature from cobalt(II) acetate (2.0 mmol./l.) and sodium iodide (0.10 mol./l.); (b) is that of $[Co(AcO)_4]$*4^{2-} formed at 150°C from cobalt(II) acetate (6.0 mmol./l.) and lithium acetate (0.10 mol./l.), and (c) is that of the hexaquo cobalt(II) ion $[Co(H_2O)_6]^{2+}$ (6.0 mmol./l.) in water.

Tetrahedral cobalt(II) complex ions of the $[CoX_4]^{2-}$ type, where X is AcO^-, NCS^-, Cl^-, Br^- or I^-, have absorptions in a visible range, their extinction coefficients being about one hundred times stronger than that of the hexaquo cobalt(II) ion. According to the ligand field theory,[8] their absorptions are due to the electronic transitions of $d_\gamma \rightarrow d_\varepsilon$. The decrease in the strength of a ligand field decreases the difference between d_γ and d_ε; the absorption, therefore, shifts toward longer wavelengths. The absorption spectra of $[CoX_4]^{2-}$ are represented in Table I. The decrease in the strength of a ligand field becomes larger in the order of AcO^-, NCS^- Cl^-, Br^- and I^-.

I, II and III of Fig. 1 show that the absorption corresponding to that of $[CoI_4]^{2-}$ obviously increases with the increase in the amount of iodide ions added. The extinction coefficient of $[Co(AcO)_4]^{2-}$ ($\varepsilon=1700$) is larger than that of $[CoI_4]^{2-}$. It seems, therefore, unreasonable that the absorption corresponding to $[CoI_4]^{2-}$ becomes stronger than that corresponding to $[Co(AcO_4)]^{2-}$. It is considered that those complex ions that have methanol, acetic acid or water as the ligand L are present in considerable quantities, together with $[Co(AcO)_4]^{2-}$, although it is nearly impossible to distinguish their absorption spectra from those of $[Co(AcO)_4]^{2-}$ and $[Co^{2+}(L)_6]$. Their extinction coefficients are probably smaller than that of $[Co(AcO)_4]^{2-}$. Therefore, the absorption corresponding to $[Co(AcO)_4]^{2-}$ recorded in Fig. 2 is not as strong as expected.

The variation in the absorption spectra may be divided into three parts. The first part lasts for about 20 min. after the temperature has reached 180°C, within which period no variation in the absorption of cobalt(II) ion is observed except that the absorption in the short-wavelength region gradually decreases. The second part lasts from about 20 to 100 min., within which period, as soon as the absorption from 500 to 650 mμ has started decreasing, that from 600 to 800 mμ goes on increasing until it reaches its maximum. The third part lasts from about 100 to 300 min., within which period the variation is the inverse of that of the second part. The absorption spectrum recorded after 200 to 300 min. becomes nearly the same as that of the first part. In the case of IV, the absorption from 500 to 650 mμ decreases very much within 25 min. after the temperature reaches 180°C; however, that from 600 to 800 mμ scarcely increases at all, and no variation is observed after 25 min. These are large differences from I, II and III.

The present authors would like to give the following estimates of these three parts of the variation. In the first part, most of the iodine molecules formed from iodide ions have been

*4 The octahedral species of the $[Co^{2+}(L)_6]$ type, where L represents AcO^-, AcOH or H_2O, are present in considerable quantities, together with $[Co(AcO)_4]^{2-}$.

8) L. E. Orgel, "An Introduction to Transition Metal Chemistry (Ligand Field Theory)," Methuen & Co. Ltd., London (1960).

reduced to iodide ions once again,*5 and the reaction does not start (an induction time). The second part is that in which the reaction starts and its rate reaches its maximum. The third part is that in which the partial pressure of carbon monoxide decreases in proportion as the reaction proceeds, until it nearly stops after 200 to 300 min. These estimates are supported by the following experimental results.

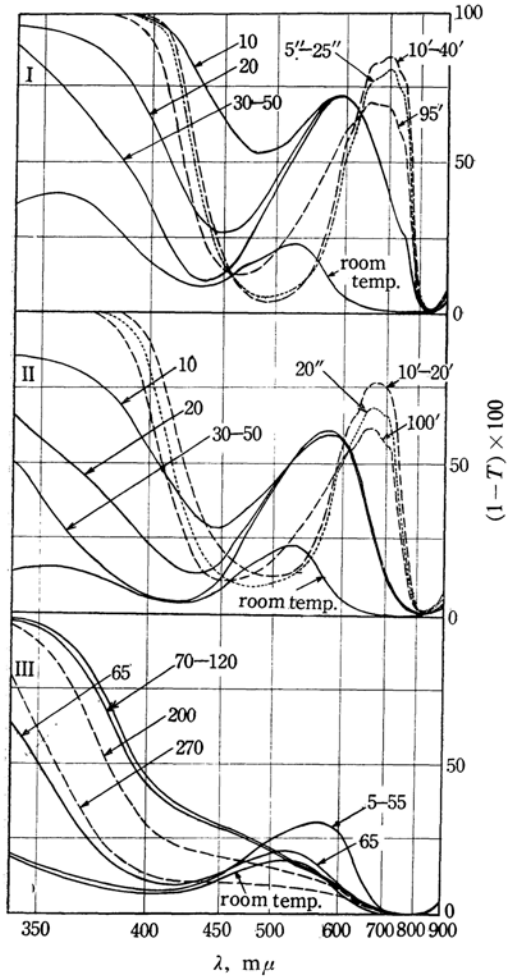

Fig. 3. The variation in the absorption spectra in course of the reaction under 200—220 kg./cm² ($CO/H_2=1$) at 185°C.
(I) $I^-/Co^{2+}=10$, (II) $I^-/Co^{2+}=2$ and (III) $I^-/Co^{2+}=0$. Numbers in the figure are the time (min.) since the temperature of the autoclave has reached 185°C and dashed numbers (t' and t'') are those since the higher pressure gases have been introduced up to 220 kg./cm² at 185°C.

*5 The absorption in the short wavelengths is observed to decrease. See the near ultraviolet absorptions recorded in I and II of Fig. 3. It may be considered that most of the iodine molecules are formed according to the following reactions:

$$I^- + AcOH \rightleftarrows AcO^- + HI, \quad 2HI \rightleftarrows H_2 + I_2$$

The gases ($CO/H_2=1$) with a lower pressure (60 kg./cm²) than that in Fig. 2 were introduced at room temperature into the autoclave, in which the same solution as that of II in Fig. 2 had previously been placed. After the temperature had been kept constant at 185°C for about one hour (the variation in the absorption spectra within this period is shown by the full lines in I and II of Fig. 3), higher-pressure gases ($CO/H_2=1$) were introduced up to 220 kg./cm² at this temperature and the absorption spectra were taken (the broken lines). The results are summarized as I in Fig. 3. When the higher-pressure gases were introduced, most of the iodine molecules formed had already been reduced to iodide ions. The reaction, therefore, starts without exhibiting any induction time; the absorption from 600 to 800 mμ goes on increasing so fast that it reaches its maximum after about 10 min. After about 3 hr., the absorption spectrum returns to become nearly the same as it was before the reaction started. It may be expected that, if the higher pressure gases are once more introduced up to 220 kg./cm², nearly the same variation will again be observed. This is shown by the dotted lines in Fig. 3. II of Fig. 3 shows the results obtained when a small number of iodide ions are present in the solution ($I^-/Co^{2+}=2$).

These experimental results show that the reaction of methanol with carbon monoxide-hydrogen starts at the time that the iodine molecules formed have been mostly reduced to iodide ions, and that it is accompanied by an increase in the number of tetrahedral iodocobalt(II) complex ions.

Near Ultraviolet Absorption Spectra.—There may be expected to be five kinds of absorptions in a near ultraviolet region. 1) The absorption of an iodine. The strong absorption of an iodine molecule takes place from a visible part to a near ultraviolet one. This is due to the transition of non-bonding electrons in the iodine molecule ($n \rightarrow \sigma^*$).[9] This absorption is observed from 600 mμ toward the near ultraviolet region*6 of these absorption specra that are taken immediately after the temperature of the autoclave has reached 185°C (I and II of Fig. 3). 2) An electronic charge transfer from a coordinated iodine ion to the cobalt(II) ion. Whenever the reaction starts and the number of iodo-cobalt(II) complex ions increases, a new strong absorption takes place from 480 mμ to the shorter wavelengths, as is shown in I and II of Fig. 3. This absorption is probably due to an electronic charge

9) C. N. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths, London (1961).

*6 This was confirmed by a preliminary experiment.

transfer of the $Co^{2+} + I^- \rightarrow Co^+ + I$ type, which may be correlated with the oxidation-reduction potential of cobalt(II) ions.[7] 3) An electronic charge transfer of the Mulliken type. If an iodine molecule or an iodide ion makes a weak bond with a solvent molecule, it may be expected that an electronic charge transfer of the Mulliken type[10] will take place in a near ultraviolet region. 4) The absorptions of cobalt carbonyls. III of Fig. 3 shows the variation in the absorption spectrum of the solution (methanol 9 : acetic acid 1) containing only cobalt(II) acetate (0.020 mol.%) under the same conditions as those of I, II and III of Fig. 2. After 50 to 60 min. since the temperature has been increased up to 180°C, the absorption corresponding to that of $[Co(AcO)_4]^{2-}$ decreases rapidly, while a new strong absorption takes place in the near ultraviolet region, although its intensity continues to decrease. This new absorption may be considered to be that of the cobalt carbonyl*7 formed from the following equations: $Co^{2+} + H_2 \rightarrow Co + 2H^+$, $2Co + 8CO \rightarrow Co_2(CO)_8$, $H_2 + Co_2(CO)_8 \rightarrow 2HCo(CO)_4 \rightarrow 2H^+ + 2[Co(CO)_4]^-$; it may also be considered that its decomposition into metallic cobalt[11] causes its absorption to decrease. 5) The absorption of acetaldehyde. Acetaldehyde formed has an absorption from 330 mμ to the shorter wavelengths ($n \rightarrow \pi^*$, $\varepsilon = 10$—100). However, the intensity of the near ultraviolet absorption due to the electronic charge transfer from iodine ions to cobalt(II) ions was so strong that it was difficult to confirm the formation of cobalt carbonyls during the course of the reaction.

From the variation in the visible absorption spectra of cobalt(II) ions in the course of the reaction of methanol with carbon monoxide and hydrogen, it may be considered that, when a comparatively large number of iodide ions are added to the solution, most of the cobalt(II) ions do not form cobalt carbonyls, but tetrahedral cobalt(II) complex ions, and that the equilibrium of the equation represented apparently by $[Co(AcO)_{4-n}I_n]^{2-} + I^- \rightleftarrows [Co(AcO)_{3-n}I_{n+1}]^{2-} + AcO^-$ inclines much toward the right side in the course of the reaction. This is greatly different from an oxo-reaction.

10) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

*7 This absorption is estimated to be the transition of the bonding electrons between a cobalt atom and carbon monoxides to an anti-bonding orbital (H. B. Gray et al., *J. Am. Chem. Soc.*, **84**, 3404 (1962); R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963)).

11) P. H. Emett, "Catalysis," Vol. V. Reinhold Publ. Corp., New York (1957), p. 73.

Summary

The absorption spectra during the course of the reaction of methanol with carbon monoxide-hydrogen mixtures in the presence of a mixture of cobalt(II) acetate and sodium iodide as the catalyst under high temperatures and pressures (180—185°C, 200—220 kg./cm^2) have been taken, using an automatic recording spectrophotometer and special autoclave made of Ti-Mn alloy and a couple of thick pieces of quartz glass. Whenever the reaction starts, the absorption corresponding to that of $[Co(AcO)_4]^{2-}$ goes on decreasing, while that corresponding to $[CoI_4]^{2-}$ increases in place. It has been difficult to confirm the formation of cobalt carbonyls as $Co_2(CO)_8$ and $HCo(CO)_4$ during the course of the reaction, because their absortions overlap with those of the strong electronic charge transfer of tetrahedral iodocobalt(II) complex ions. From the experimental results and subsequent considerations, it has been shown that, when a comparatively large number of iodide ions are present in the solution, most of the cobalt(II) ions do not form cobalt carbonyls, but tetrahedral cobalt(II) complex ions of the $[Co(AcO)_{4-n}I_n]^{2-}$ type ($n = 1$—4) during the course of the reaction, and that the reaction is accompanied by an increase in the number of tetrahedral iodocobalt(II) complex ions.

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Government Chemical Industrial Research Institute, Tokyo
Meguro-ku, Tokyo