Chemiluminescence from the Reaction of Singlet Oxygen with 10,10′-Dimethyl-9,9′-biacridylidene. A Reactive 1,2-Dioxetane

Kyu-Wang Lee and Lawrence A. Singer*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

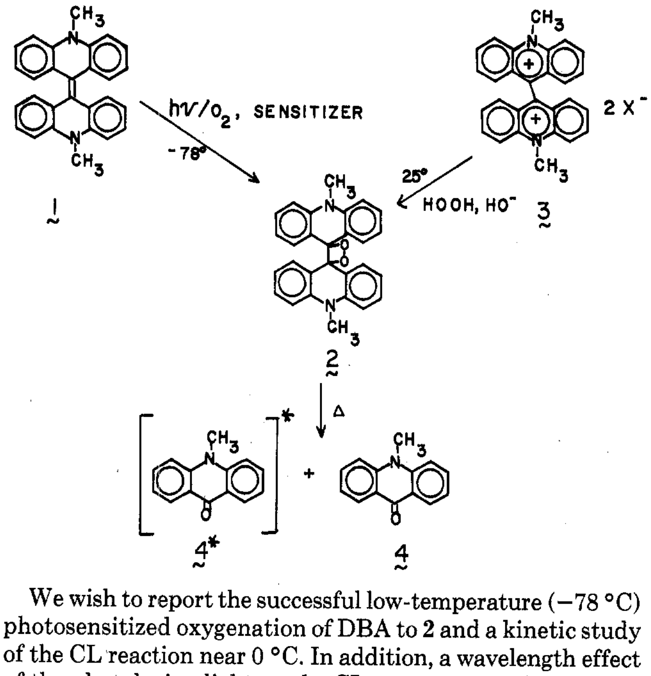
Kenneth D. Legg[1]

Department of Chemistry, California State University, Long Beach, Long Beach, California 90840

Received February 5, 1976

Irradiation of 10,10′-dimethyl-9,9′-biacridylidene (DBA) in several oxygen saturated solvents at −78 °C in the presence of zinc tetraphenylporphine leads to the corresponding 1,2-dioxetane (**2**). While **2** is stable at −78 °C, it decomposes into two molecules of *N*-methylacridone (NMA) at higher temperatures ($\tau_{1/2} \sim 1$ min at 0 °C) with light evolution (NMA fluorescence). The activation parameters have been measured to be dichloromethane, $\Delta H^{\ddagger} = 17.2 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -1.1 \pm 1.1$ eu; benzene, $\Delta H^{\ddagger} = 16.7 \pm 0.2$ kcal/mol, $\Delta S^{\ddagger} = -5.0 \pm 2.1$ eu; pinacolone, $\Delta H^{\ddagger} = 18.2 \pm 0.3$ kcal/mol, $\Delta S^{\ddagger} = -1.4 \pm 1.2$ eu. The chemiexcitation quantum yield for formation of ^{1}NMA* is 0.036 ± 0.018 for the photooxygenation ($\lambda_{\text{excitation}} > 550$ nm) or triphenyl phosphite ozonide oxidation of DBA. However, photooxygenation using unfiltered light gives quantum yields lower by a factor of 20 which is ascribed to photoinduced decomposition of **2**. The quantum yield for formation of ^{3}NMA* has been measured as 0.04 ± 0.01.

1,2-Dioxetanes have been recognized as important intermediates in chemiluminescence reactions[2] and in alkene photooxygenations.[3] McCapra and Hann[4] reported chemiluminescence (CL) from reaction of singlet ($^1O_2$) oxygen (from triphenyl phosphite ozonide, $Br_2/H_2O_2/OH^-$, and rf discharge) with 10,10′-dimethyl-9,9′-biacridylidene (DBA, **1**), presumably arising from the thermal decomposition of a 1,2-dioxetane intermediate, **2**. This compound has been proposed as the key intermediate in the "classical" CL reaction of lucigenin (**3**).[5]



We wish to report the successful low-temperature (−78 °C) photosensitized oxygenation of DBA to **2** and a kinetic study of the CL reaction near 0 °C. In addition, a wavelength effect of the photolyzing light on the CL quantum yield (*N*-methylacridone and DBA fluorescence) was noted. For comparison, the CL quantum yield from **2**, produced via reaction of $^1O_2$, generated from decomposition of triphenyl phosphite ozonide ($TPPO_3$), with DBA has been determined. Finally, the quantum yield for formation of *N*-methylacridone triplet from decomposition of **2** has been determined.

Results and Discussion

Photooxygenation of DBA in various solvents at −78 °C is readily accomplished by irradiating an oxygen-saturated solution of DBA ($\sim 2 \times 10^{-4}$ M)[6] with visible light in the presence of zinc tetraphenylporphine (ZnTP) (10^{-4}–10^{-5} M).[7,8] A low-level, self-sensitized reaction is observed in the absence of sensitizer[9] but the sensitizer increases the yield of the reaction by at least two orders of magnitude. Contrary to an earlier report,[4] no CL is observed following reaction at −78 °C while the low temperature is maintained. However, a bright CL is observed as the sample is warmed toward room temperature, which we ascribe to the decomposition of **2** by analogy with similar systems.[3]

Our results confirm previous reports that *N*-methylacridone (NMA, **4**) is the primary emitter in the CL reaction, the emission being NMA fluorescence[4] (see Figure 1). Under conditions of high remaining DBA concentration (i.e., incomplete reaction, DBA $\geq 10^{-4}$ M), a significant amount of the emission is DBA fluorescence produced via singlet–singlet energy transfer from NMA:[10] $^1\text{NMA}^* + \text{DBA} \rightarrow \text{NMA} + {}^1\text{DBA}^*$. Reaction of DBA with $^1O_2$ produced from the decomposition of $TPPO_3$ gave similar CL spectra.

Kinetics. The rates of thermal decomposition of **2** in several solvents at various temperatures have been determined by directly monitoring the CL decay. After the sample reached thermal equilibrium following warmup from −78 °C, the CL decay was first order out to ca. 3 half-lives. The CL decay is independent of sensitizer concentration over the concentration range used. As a check, methylene blue was used as a sensitizer and gave identical kinetic results. The derived activation parameters appear in Table I.

As previously noted,[11] there is an appreciable effect of trace impurities on the kinetics. Column chromatography over silica gel proved effective in purifying dichloromethane (see Table I). Saturating pyridine with disodium ethylenediaminetetraacetic acid (EDTA) did not prove to be totally effective in eliminating the impurity effect on the kinetics (see Table I).

Note that our kinetic data predict a relatively short lifetime ($\tau_{1/2} \sim 7$ s) for **2** at room temperature which is consistent with it being a short-lived intermediate during the lucigenin/H_2O_2/HO^- reaction.[5] This reactivity of **2** is generally greater than that of many previously reported 1,2-dioxetanes of alkenes,[12–14] but appears comparable to the reactivity reported for 1,2-dioxetanes derived from enamines.[15,16]

Chemiexcitation Quantum Yields. Chemiexcitation quantum yields (see footnote *a*, Table II) of electronically excited singlet state formation, $^1\Phi_{CE}$, were determined by

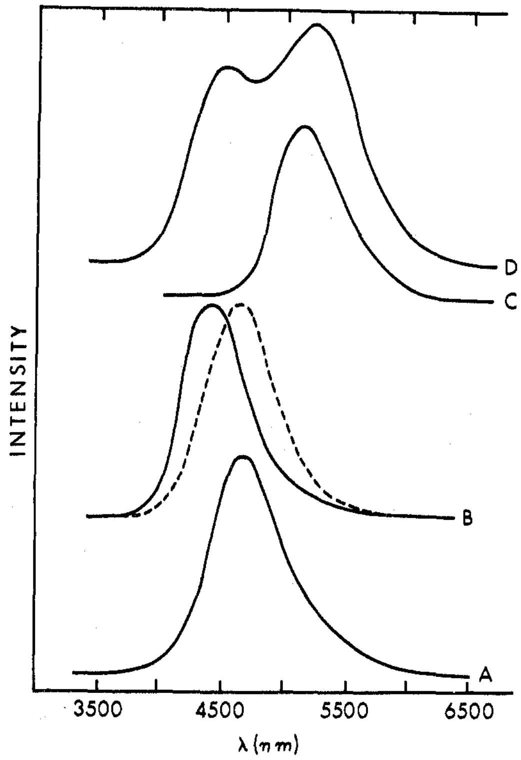


Figure 1. Chemiluminescence during warmup after $^1O_2$ reaction with DBA at −78 °C: (A) normalized fluorescence spectrum of NMA in the absence (B—) and presence (B - - -) of ZnTP (10^{-4} M). Fluorescence spectrum of DBA in the presence (C) of ZnTP (10^{-4} M). Chemiluminescence from incomplete reaction of DBA with $^1O_2$ (D). The shift in (B - - -) is due to internal absorption of high-energy side of emission band by ZnTP.

assaying specific runs for both NMA formed and photons emitted. Product yields were determined from fluorometric assay with known concentrations of NMA as internal standards by the method of standard additions. This technique allows accurate measurement of the NMA concentration after reaction, since any fluorescence quenching that might occur will affect both the unknown and standard equally. Photon yields were photometrically determined relative to the luminol–hemin–H_2O_2 reaction which served as an absolute photon source.[17] Because of the spectral similarity of the CL's from the luminol reaction and decomposition of **2**, a correction for photomultiplier response was not necessary. These yields are shown in Table II. The values of Φ_f for NMA were determined under aerated condition which mimics the situation during the CL reaction.

As a check, the $^1\Phi_{CE}$ for the $TPPO_3$ reaction was measured (Table II). The discrepancy in $^1\Phi_{CE}$ of ca. 20 between the two reactions led to a study of possible complications in the photooxygenation reaction. The lower $^1\Phi_{CE}$ in the latter appears not to be due to the presence of the sensitizer since the CL kinetics are independent of sensitizer concentration and quenching of the NMA fluorescence by the sensitizer under our conditions is negligible. However, we did note *decreasing* relative light yields[18] with *increasing* photolysis time. The self-sensitized photooxygenation reaction showed the same results.

These observations suggested that the reduced light yields in the photooxygenation reactions were a result of the direct photodecomposition of **2** during the photolysis and/or a sensitized decomposition via DBA*. The absorbance of DBA extends to ca. 500 nm and **2** should not absorb at longer wavelengths. Accordingly, a Corning CS 3-67 filter (550 nm short wavelength cutoff) was placed between the light source and the photolysis Dewar. With this filter in place, the relative light yields were found to increase with photolysis time, indicating stability of **2** under these conditions. The $^1\Phi_{CE}$ thus obtained compares favorably (see Table II) with that measured for the $TPPO_3$ reaction and we consider this a good (±50%) estimate of the ^{1}NMA* yield for the decomposition of **2**.

The sensitized *trans* → *cis*-stilbene reaction was used as a probe for counting the ^{3}NMA* yield. Irradiation (366 nm) of an aerated dichloromethane solution of *trans*-stilbene (1.0×10^{-2} M) containing NMA (1.0×10^{-3} M) showed efficient interception of the ^{3}NMA* by *trans*-stilbene with a sensitization quantum efficiency of essentially unity for the trans → cis isomerization (ferrioxalate actinometry, accounting for $\Phi_{ISC} \sim 0.56$ in NMA from $\Phi_{ISC} = 1 - \phi_f$). Singlet–triplet and singlet–singlet energy transfer are ruled out since *trans*-stilbene does not quench the fluorescence of NMA. For the counting experiment, scintillation grade *trans*-stilbene was further purified by preparative gas chromatography yielding a sample containing $\lesssim 0.02\%$ *cis*-stilbene. This purified *trans*-stilbene (1.0×10^{-2} M) was added to a dichloromethane solution of DBA–$TPPO_3$ at −78 °C (conditions the same as in the CL quantum yield experiment) and the mixture allowed to warm to room temperature. Gas chromatography indicated an enrichment of the *cis*-stilbene over the starting stilbene mixture.[19] From the *cis*-stilbene yield, we estimate the quantum yield for formation of ^{3}NMA* to be 0.04 ± 0.01, assuming triplet sensitization to be completely efficient.[20] The expected quantum yield for ^{3}NMA* arising from intersystem crossing of ^{1}NMA* alone is 0.02 ± 0.01 ($\Phi_{^3NMA^*} = {}^1\Phi_{CE} \times \Phi_{ISC}$).

In summary, we have found that (1) the kinetics of the decomposition of **2** are relatively solvent independent in aprotic solvents in the absence of impurity effects, (2) the $^1\Phi_{CE}$ is relatively high leading to substantial CL, comparable to the CL from luminol[17] and lucigenin which are considered high CL systems and (3) the quantum yield for formation of ^{3}NMA* is within experimental error of that expected from intersystem crossing of the chemiexcitation produced ^{1}NMA*.[21] Because of the intrinsically large Φ_f of NMA, potential chemiluminescent systems modeled so as to yield NMA appear highly desirable. Further work along this line is in progress. We also would like to add a note of precaution to others about measuring CL quantum yields from dioxetanes produced *only* by photooxygenation because of the photoinduced decomposition of **2**.

Experimental Section

Materials. Benzene (Mallinckrodt, reagent grade) was distilled through a 20-in. fractionation column and a middle cut was taken. Pyridine (Mallinckrodt, reagent grade) was dried over potassium hydroxide and then fractionally distilled from potassium hydroxide under N_2. Dichloromethane (Mallinckrodt, reagent grade) was purified by filtering through silica gel (Baker, analyzed reagent). Pinacolone (MCB, reagent grade) was fractionally distilled through a 14-in. column and a center cut was collected. Hemin chloride (Calbiochem) and luminol (Aldrich) were used as received.

Synthesis. 10,10′-Dimethyl-9,9′-biacridylidene (1) was prepared by zinc reduction of lucigenin (**3**).[22] The product was purified either by dry-column chromatography on alumina or by recrystallization from pyridine, mp > 360 °C. **1** was assessed pure when a uv–visible absorption spectrum was obtained identical with that reported in the literature.[10]

***N*-Methylacridone (4)** was obtained by N-methylation of acridone using excess methyl iodide in the presence of potassium hydroxide in ethanol–acetone and also from dry-column chromatography of the product of the lucigenin/H_2O_2/HO^- reaction.[5] Acridone was prepared by the method of Allen and McKee.[23]

Zinc Tetraphenylporphine (ZnTP). Into a 300-ml round-bottom flask arranged for magnetic stirring was placed 0.45 g (0.73 mmol) of tetraphenylporphine,[25] 0.32 g (1.46 mmol) of zinc acetate, and 100 ml of dry dimethylformamide. The mixture was refluxed for 1 h. The course of the reaction was monitored by uv–visible absorption spec-

Table I. Thermal Decomposition of Dioxetane 2

Solvent	E_a, kcal mol^{-1}	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] eu	K dec (0 °C), s^{-1}
CH_2Cl_2	12.5 (±1.0)	11.9 (±1.0)	−20.3 (±3.7)	0.056 (±0.0006)
CH_2Cl_2 (after column)	17.8 (±0.3)	17.2 (±0.3)	−1.1 (±1.1)	0.056 (±0.006)
Pinacolone	18.7 (±0.3)	18.2 (±0.3)	−1.4 (±1.2)	0.008 (±0.001)
Pyridine	4.0 (±0.6)	3.4 (±0.6)	−55.7 (±2.3)	0.004 (±0.0005)
Pyridine (EDTA)	11.8 (±1.6)	11.3 (±1.6)	−28.5 (±5.9)	0.007 (±0.0005)
Benzene	17.2 (±0.2)	16.7 (±.02)	−5.0 (±2.1)	0.020 (±0.002)

[a] Calculated for 0 °C.

Table II. Light Yields from $^1O_2$ Reaction[a]

Solvent	Φ_{CL}	Φ_f[b]	Φ_{CE}
Pinacolone[c]	6.2×10^{-4}	0.28	2.2×10^{-3}
Pyridine[c]	9.6×10^{-4}	0.34	2.8×10^{-3}
Dichloromethane[c]	7.7×10^{-4}	0.44	1.8×10^{-3}
Dichloromethane[d]	1.60×10^{-2}	0.44	3.61×10^{-2}
Dichloromethane[e]	1.55×10^{-2}	0.44	3.52×10^{-2}

[a] Φ_{CL} = (Einsteins of light)/(moles of NMA produced); $\Phi_{CE} = \Phi_{CL}/\Phi_f$. In a typical run, the NMA yield by fluorometric assay indicated 25–50% consumption of DBA. [b] All under aerated conditions. All measured relative to the quantum yield for NMA fluorescence in aerated ethanol, $\Phi_f = 0.61$, ref 9. [c] Photogeneration of $^1O_2$ using unfiltered light. [d] Photogeneration of $^1O_2$ using CS 3-67 filter. [e] $^1O_2$ via decomposition of triphenyl phosphite ozonide from ozonation of ca. 0.1 M TPP at −78 °C.

troscopy. When the reaction was complete, as judged by the characteristic absorption bands of the product,[26] the mixture was cooled to room temperature and 100 ml of benzene and 50 ml of water were added. The organic layer was separated and the aqueous layer was extracted twice with 100 ml of benzene. The combined benzene layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The product was recrystallized from a 1:1 mixture (v/v) of chloroform/carbon tetrachloride to yield shiny violet plates. The yield was ca. 95%.

Triphenyl phosphite ozonide ($TPPO_3$)[24] was prepared by passing a stream of O_3 (Welsbach ozonator, Model T-408) into a solution of freshly distilled triphenyl phosphite (0.10 M) in dichloromethane at −78 °C until the development of an iodine color in an aqueous KI trap which was placed after the reaction flask. The cold solution was purged with dry N_2 for at least 0.5 h to ensure removal of traces of O_3.

***trans*-Stilbene** (Matheson, scintillation grade, 99.8%) was further purified by preparative gas chromatography using a Hewlett-Packard Model 402B gas chromatograph fitted with a 20% Carbowax on Chromosorb P column at 135 °C. The *trans*-stilbene thus obtained contained <0.02% *cis*-stilbene as determined by flame ionization gas chromatography on the above instrument.

Procedures. Photooxygenations. Aerated samples of DBA (1, $\sim 10^{-4}$ M) in 7-mm diameter Pyrex tubes were placed in a silvered Dewar equipped with a 2 × 2 in. Pyrex window and irradiated with a Sylvania DWY tungsten iodine lamp (650 W) for ~20 min at −78 °C. When appropriate, as described under Results and Discussion (Table II), a Corning CS-3-67 filter (550-nm short wavelength cutoff) was inserted between the light source and the sample.

Chemiluminescence Spectra. CL spectra were obtained on an American Instrument Co. spectrofluorometer equipped with an IP-21 photomultiplier tube. A clear Pyrex Dewar was put in place of the usual sample holder. The tube containing the photooxygenated solution, or a mixture of DBA and $TPPO_3$, at −78 °C was placed in the Dewar (25 °C) and the CL spectra were immediately recorded during warmup of the samples using a 5-mm slit on the exit of the scanning 0.25-m monochromator (Figure 1). Note that under these low-resolution conditions, the characteristic double peak of NMA fluorescence[10] is not seen.

Kinetic Data. The total CL decay was monitored from photooxygenated samples held at constant temperature in a clear Pyrex Dewar placed immediately in front of the entrance slit to the photomultiplier housing. The samples were introduced into the Dewar in a rigid, reproducible geometry and CL decay curves were obtained over at least 3 half-lives following thermal equilibrium.

Chemiluminescence Quantum Yields. The light yields were measured using the same sample cell configuration as under kinetic data. Photooxygenated or $TPPO_3$–DBA samples were transferred from the −78 °C bath to the sample Dewar (25 °C) and the total light vs. time curves were recorded. Photon yields of emission were determined by comparing the areas under the above CL decays with similar curves obtained from the standardized luminol–hemin–H_2O_2 reaction[17] run in exactly the same geometry. Because of the similarity in the emission spectra from the two systems, no correction for photomultiplier response was needed.

NMA yields were determined by the method of standard additions. The reaction mixture was divided into five equal portions and to each was added a different concentration of a standardized NMA solution. The fluorescence from each solution was recorded. The unknown NMA concentration was determined by plotting fluorescence intensity vs. concentration of added NMA and extrapolating to zero concentration of added NMA. The intercept provides the fluorescence intensity of the unknown NMA and the slope provides the constant relating fluorescence intensity to concentration. Typically, the solutions initially were $1–2 \times 10^{-4}$ M in DBA and the NMA formed was $2–3 \times 10^{-4}$ M indicating 75–100% consumption of DBA.

The quantum yields were calculated from Φ_{CL} = (Einsteins of light)/(moles of NMA produced) and the chemiexcitation quantum yield is given by $\Phi_{CE} = \Phi_{CL}/\Phi_f$. The Φ_f was independently determined under aerated conditions by comparison of the fluorescence from the NMA solutions with that from NMA in aerated ethanol, $\Phi_f = 0.61$.[10]

Note that the CL spectra shown in Figure 1 were run in the presence of 1.0×10^{-4} M ZnTP. Under those conditions, a noticeable shift in the NMA fluorescence is observed probably due to reabsorption of the high-energy shoulder by ZnTP which absorbs strongly near 425 nm (422 nm, ϵ 60000).[26] The above light yields were determined in the presence of $\sim 10^{-5}$ M ZnTP to minimize the reabsorption problem. The similarity of the Φ_{CL} under filtered conditions with the $TPPO_3$ result (Table II) is encouraging on this point.

NMA Triplet Yield. The sensitized *trans* → *cis*-stilbene isomerization reaction[27] was used to measure the yield of $^3NMA^*$. An aerated solution of NMA (1.0×10^{-3} M) and *trans*-stilbene (99.8%) (1.0×10^{-2} M) was irradiated at 366 nm using a 150-W Xe–Hg arc in conjunction with a 0.25-m American Instrument Co. monochromator. The *cis*-stilbene yield was determined by flame ionization gas chromatography analysis as described above. The photons absorbed were determined by conventional ferrioxalate actinometry. The quantum efficiency for the isomerization was $\Phi_{t\rightarrow c} \sim 1$ after accounting for the singlet to triplet intersystem crossing efficiency of NMA, $\phi_{isc} \sim 0.56$ (from $\phi_{isc} = 1 - \Phi_f$). The apparently very low phosphorescence yield of $^3NMA^*$ precluded measuring $^3\Phi_{CE}$ by direct spectroscopic techniques.[28]

The triplet counting experiment was performed by adding the ultrapure *trans*-stilbene (99.98%) (1.0×10^{-2} M) to a dichloromethane solution of $TPPO_3$–DBA at −78 °C. The mixture was allowed to warm up to room temperature. The *cis*-stilbene content of this solution (7.7×10^{-6} M) was measured by flame ionization gas chromatography under conditions described above. The background *cis*-stilbene was 2×10^{-6} M. The NMA yield was determined by fluorescence assay as described above as 1.95×10^{-4} M.

Acknowledgment. We thank the U.S. Army Research Office, Durham, for partial support of this work.

Registry No.—**1**, 23663-77-6; **2**, 59230-86-3; **3**, 2315-97-1; **4**, 719-54-0.

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(19) A control experiment showed that warmup from −78 °C of a dichloromethane solution containing *trans*-stilbene (10^{-2} M) and $TPPO_3$ yielded no detectable increase in *cis*-stilbene over that initially present.

(20) Photolysis at 366 nm of this same reaction mixture yielded additional *cis*-stilbene with near unit quantum efficiency indicating that the products of the DBA–$TPPO_3$ reaction are not inhibitors of the stilbene sensitized isomerization. Hence the ^{3}NMA* counting experiment result is not in need of upward revision.

(21) From the other end of our error limits, we obtain $^1\Phi_{CE} = 0.018$ and Φ of ^{3}NMA* = 0.05 with the *maximum yield of directly formed* NMA* (excluding that from intersystem crossing) being $^3\Phi_{CE} = 0.04$. In view of the relatively large singlet–triplet splitting in NMA (probably $\gtrsim 10$ kcal/mol) we conclude that energetics are not dominating the competition between the chemiexcitation pathways directly leading to singlet and triplet NMA. The extent to which this result depends on the π,π^* nature of the low-lying excited states of NMA needs further elucidation.

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Transfer Hydrogenation and Transfer Hydrogenolysis. 11. Facile Dehydrogenation of Aromatic Hydrocarbons and the Mechanism of the Hydrogen Transfer from Indan, Tetralin, and Dioxane to Aldehydes Catalyzed by Dihydridotetrakis(triphenylphosphine)ruthenium(II)

Hideaki Imai,* Takeshi Nishiguchi, and Kazuo Fukuzumi

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

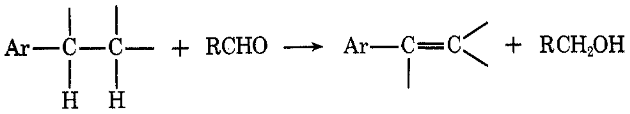
Received March 2, 1976

Aromatic hydrocarbons, such as indan and ethylbenzene, were dehydrogenated and reduced aldehydes under mild conditions in the presence of $RuH_2(PPh_3)_4$. It was also found that indan and isobutylbenzene reduced cycloheptene under more drastic condition in the presence of $RhCl(PPh_3)_3$. The mechanism of hydrogen transfer from indan, tetralin, and dioxane to an aldehyde catalyzed by $RuH_2(PPh_3)_4$ was investigated, and found to be different from that of the reduction of aldehydes by alcohols. The transfer hydrogenation by the aprotic substances occurs via dihydride complexes, and the overall rate law was rate = $a[DH_2][cat.]_0/(1 + b[DH_2] + c[RCHO])$ where $[DH_2]$, $[cat.]_0$, and [RCHO] are hydrogen donor, added catalyst, and aldehyde concentrations, respectively. The rate-determining step of the reduction by the aprotic hydrogen donors is the hydrogen transfer from the donors to the catalytic species.

In the catalytic transfer hydrogenation of carbonyl compounds, only primary and secondary alcohols[1] and formic acid[2] have been reported to donate hydrogen atoms under rather drastic conditions. We previously reported that ethers and hydroaromatic compounds also reduced aldehydes and ketones, and discussed the mechanism of the hydrogen transfer from alcohols to aldehydes catalyzed by $RuH_2(PPh_3)_4$.[3] Later, we found that aromatic hydrocarbons also gave hydrogen to aldehydes under mild conditions and to olefins under more drastic conditions. This study was undertaken to investigate the difference between the mechanism of the transfer hydrogenation of aldehydes by the protic hydrogen donors, alcohols, and that of the one by aprotic donors such as indan, tetralin, and dioxane.

Results and Discussion

Hydrogen-Donating Ability of Aromatic Hydrocarbons. Although the dehydrogenation of aromatic hydrocarbons has been carried out under drastic conditions in the presence of heterogeneous catalysts, we found that the dehydrogenation occurred under mild conditions with homogeneous catalysts. When an aromatic hydrocarbon (2.0 M), *n*-hexaldehyde (1.0 M), and $RuH_2(PPh_3)_4$ (0.02 M) were heated in bromobenzene at 36.5 °C, *n*-hexyl alcohol and a



$$\mathrm{Ar{-}\underset{H}{\overset{|}{\underset{|}{C}}}{-}\underset{H}{\overset{|}{\underset{|}{C}}}{-}} + \mathrm{RCHO} \longrightarrow \mathrm{Ar{-}\underset{|}{C}{=}C\!<} + \mathrm{RCH_2OH}$$