Catalytic Oxidation with Nitrous Oxide: Oxidation of Alcohols, Ethers and Amines in an Aqueous Suspension of Platinum Particles at Room Temperature

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Room-temperature catalytic oxidation of alcohols, ethers and amines with nitrous oxide (N_2O) has been performed, along with nitrogen (N_2) evolution, in aqueous suspensions of platinum black (Pt). Appreciable decomposition of N_2O to give N_2 is observed in the co-presence of Pt particles and an appropriate substrate. Ketones are obtained from secondary alcohols, amines and branched ethers, while aldehydes, along with carboxylic acids and nitriles, are produced from primary alcohols and amines, respectively. The oxidative decomposition of diisopropyl ether to yield acetone begins after an appreciable induction period, which disappears on the addition of small amount of propan-2-ol to the reaction mixture. An induction period is also observed in the oxidation of propan-2-ol carried out under neutral or alkaline conditions. However, the oxidation of another portion of propan-2-ol, added after almost complete consumption of the initial portion, occurs without an induction period. Treatment of a Pt suspension with hydrogen (H_2) is also effective for elimination of the induction period. A radical chain mechanism is proposed, in which N–O bond cleavage in N_2O adsorbed on Pt gives rise to a primary intermediate of an α-substituted alkyl radical and the resulting hydroxyl radical abstracts hydrogen from the substrate.

Catalytic oxidation of organic compounds with molecular oxygen (O_2) over metals or their oxides has been extensively studied. The most plausible reaction mechanism involves the activation of O_2 on the catalyst surface to give a superoxide anion radical ($O_2^{\cdot -}$), suboxide anion (O^-), or oxygen atom (O), which leads to hydrogen abstraction and/or insertion into the substrates.[1,2] Oxidation can be also achieved with nitrous oxide (N_2O), which undergoes decomposition into nitrogen (N_2) and O^-,[3] over several metal oxides. In contrast to the less efficient stoichiometric thermal reaction under violent conditions,[4] selective oxidation of a variety of organic compounds proceeds catalytically under mild conditions, *e.g.* conversion of ethane into ethene over molybdenum oxide (MoO_3)[5] or zinc oxide,[6] partial oxidation of methane over MoO_3,[7] oxidation of carbon monoxide to carbon dioxide over MoO_3,[8] and hydroxylation of benzene to phenol.[9,10] As in these reactions N_2O provides a different mode of oxidation and offers some advantage compared with O_2,[11] but a considerably higher temperature (>800 K) is still required.

On the other hand, N_2O is also used as a trap for hydrated electron (e^-_{aq}), the primary active species, as well as hydroxyl radical ($^\cdot OH$) generated by γ-radiolysis of water, *via* reactions (1) and (2).[12]

$$H_2O \xrightarrow{\gamma\text{-ray}} {}^\cdot OH + e^-_{aq} + H^+ \qquad (1)$$

$$N_2O + e^-_{aq} + H_2O \longrightarrow N_2 + {}^\cdot OH + OH^- \qquad (2)$$

Although the reductive decomposition of N_2O to produce $^\cdot OH$ selectively seems to be a viable method for oxidation of organic compounds at ambient temperature in aqueous solution, it is observed only under limited reaction conditions, *e.g.* by γ-radiolysis,[13] photolysis[14] or electrolysis.[15] To our knowledge, the catalytic decomposition of N_2O for oxidation in aqueous solution has not yet been reported.

The present paper shows room-temperature catalytic oxidation of organic compounds with N_2O in the presence of suspended platinum (Pt) black particles. Spontaneous decomposition of N_2O leading to the oxidation of the substrates was observed, along with N_2 evolution, while no substantial decomposition of N_2O could be observed in the absence of appropriate substrates. This Pt-catalysed oxidation was studied in detail for propan-2-ol, demonstrating a radical chain mechanism which includes the reductive decomposition of surface-adsorbed N_2O with a hydroxyalkyl radical intermediate. Features and mechanism of this catalytic oxidation are described herein.

Experimental

Materials.—Platinum black (Pt) and palladium black (Pd) supplied from Nakarai Chemicals were used without further activation. N_2O ($>99.0\%$) was supplied from Showa Electric Industries. Oxygen (O_2) and hydrogen (H_2) of $>99.99\%$ purity were purchased from Teisan. Substrates were of the best available grades from Nakarai Chemicals, Wako Pure Chemicals or Tokyo Chemical Industries. Water was passed through an ion-exchange resin and distilled before use throughout this work.

Reaction Procedure.—Phosphate buffers, the pH of which were adjusted by the addition of aqueous phosphoric acid or sodium hydroxide solutions, were used in experiments to investigate the effect of pH on the reaction rate. In a general procedure, an aqueous suspension of Pt in a Pyrex tube (16.5 mm in diameter and 180 mm in length) was purged of air with a N_2O stream for at least 20 min at room temperature. In the O_2 oxidation experiments an O_2 stream was used instead of N_2O. The tube was sealed off with a rubber septum. Substrate was injected with a micro syringe through the septum and the suspension was stirred magnetically at room temperature. In the case of solid substrates, a small amount of their aqueous solution was injected.

Analyses.—A small portion of gaseous sample was withdrawn through the septum and analysed at appropriate intervals by GC (a Shimadzu GC-4A gas chromatograph

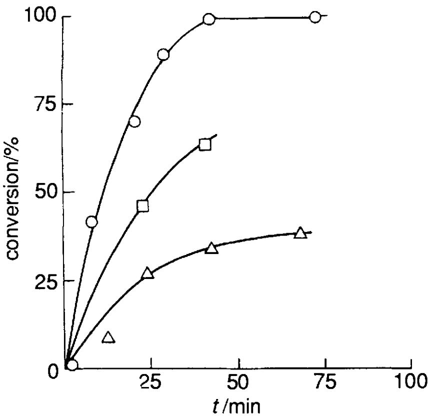

Fig. 1 Time-course of catalytic oxidation of secondary alcohols in aqueous solutions (6.5 mmol dm^{-3}, 10 cm^3; ○: propan-2-ol, □: butan-2-ol and △: pentan-2-ol) by N_2O with suspended Pt particles (2 mg). The amount of N_2O in the reaction mixture was estimated to be 0.85 mmol.

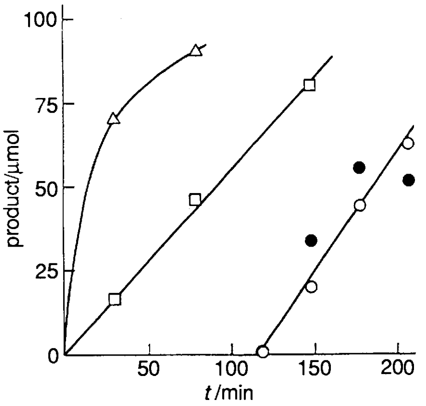

Fig. 2 Time-course of Pt (5 mg)-catalysed oxidative decomposition of di-2-propyl ether (DPE) in aqueous solution (10 mmol dm^{-3}, 10 cm^3) with N_2O (0.85 mmol) in the absence (○, ●) or presence of propan-2-ol (△: 0.065 mmol and □: 0.013 mmol). Closed and open symbols refer to yields of acetone and N_2, respectively.

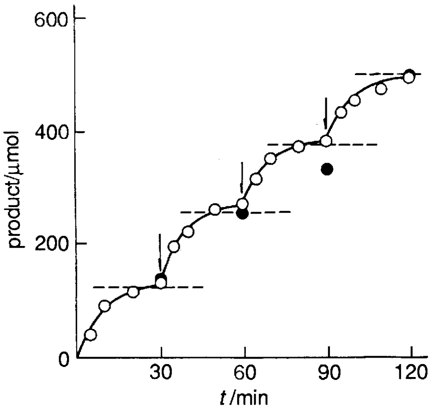

Fig. 3 Time-course of N_2 (○) and acetone (●) formation from aqueous Pt (10 mg) suspension (20 cm^3) containing propan-2-ol (0.13 mmol) in the presence of N_2O (*ca.* 20 mmol). Arrows refer to the addition of another portion of propan-2-ol (0.13 mmol). Dashed line shows the quantitative conversion of propan-2-ol.

equipped with a thermal conductivity detector with Ar carrier); a column of molecular sieve 5A (3 mm in diameter and 3 m in length) at 403 K was used for N_2 determination. After removal of Pt, the supernatant solution was subjected to GC analysis with a Shimadzu GC-6A gas chromatograph with a flame ionization detector. A column packed with 5 wt% PEG-20M on 60–80 mesh Celite 545 (3 mm in diameter and 3 m in length) was mainly used at 343–463 K with N_2 carrier. Formaldehyde,[16] ammonia,[17] oxalic acid[18] and other aliphatic carboxylic acids[19] were determined by colorimetry.

Results and Discussion

Feature of Pt-*catalysed Oxidation of Organic Compounds with* N_2O.—Table 1 shows the comparison of products of Pt-catalysed oxidation of various organic substrates with N_2O and O_2. Secondary alcohols, such as propan-2-ol or cyclohexanol, and a branched ether were oxidized to ketones in the presence of N_2O. The apparent reaction rates were higher than those under the O_2 atmosphere. Comparison of the reactivity of secondary alcohols, 2-hydroxyalkanes, under the same reaction conditions is shown in Fig. 1. Propan-2-ol was converted most readily and the reaction rate diminished with increasing length of the alkyl chain. The reactions of diisopropyl ether and propan-2-ol were studied in detail and are discussed below. Tertiary alcohol (2-methylpropan-2-ol) and amine (2-methyl-2-propylamine) were reactive with neither O_2 nor N_2O. On the other hand, the rates of consumption of primary alcohols and amines under N_2O and O_2 atmospheres were comparable. Thus, the Pt-catalysed oxidation with N_2O is effective for the substrates containing a methine carbon with a functional group substituent ($R_2CH\text{–}X$; X = OH, OR or NHR).

Oxidative Decomposition of Di-2-propyl Ether.—Representative time course of N_2 and acetone production from Pt-suspended aqueous solution of di-2-propyl ether (DPE) is shown in Fig. 2. Both products were observed after an appreciable induction period, during which the consumption of DPE was negligible. After commencement of the reaction, the DPE consumption was almost half of the formation of acetone and N_2. The stoichiometry shown in eqn. (3) is presumed.

$$[(CH_3)_2CH]_2O + 2N_2O \longrightarrow 2(CH_3)_2CO + 2N_2 + H_2O \quad (3)$$

The length of the induction period depended markedly on the reaction conditions, especially on impurities in the DPE; *e.g.*, the induction period was reduced by using freshly distilled DPE. Hydroquinone (HQ) contained in the commercial DPE (Nakarai), as an antioxidant, seems to inhibit the Pt-catalysed oxidation. In view of the well documented antioxidant action of HQ, a reaction mechanism involving hydrogen abstraction from the substrates by radical intermediates is probable.

Another interesting finding is that even in the presence of the radical stabilizer the addition of propan-2-ol to the unreactive DPE solution started the reaction effectively (Fig. 2). In this experiment, the molar amount of acetone produced exceeded that of added propan-2-ol, showing that the consumption of both propan-2-ol and DPE *via* catalytic oxidation occurs.

Pt-*Catalysed Oxidation of Propan-2-ol with* N_2O.—The evolution of N_2, as well as acetone, could be observed only in the co-presence of Pt particles and propan-2-ol; spontaneous decomposition of N_2O over Pt was negligible in the absence of appropriate substrates. The catalytic oxidation of propan-2-ol proceeded readily so that the vigorous evolution of N_2 bubbles was observed. No apparent change in the rate was observed on covering the reaction tube with aluminium foil; *i.e.* the reaction is not influenced by light. The decreased rate at the final stage (Fig. 1) was attributed to neither the deactivation of Pt nor N_2O consumption, but to the decreased concentration of propan-2-ol, since the original rate was restored by addition of another portion of propan-2-ol at the time of almost complete consumption of the initial portion (Fig. 3). This figure also shows that the ratios of products, N_2 and acetone, to the consumption of propan-2-ol were almost unity, within

Table 1 Catalytic oxidation of organic compounds with N_2O and O_2 by aqueous Pt suspension

			N_2O			O_2		
Substrate	Feed /µmol	Pt /mg	Time /h	Conv (%)	Products /µmol	Time /h	Conv (%)	Products /µmol
CH_3OH	60	2	9	17	HCHO 1, HCOOH	9	38	HCHO 1, HCOOH
CH_3CH_2OH	55	2	6	47	CH_3CHO 8, CH_3COOH	6	51	CH_3CHO 8, CH_3COOH
$CH_3CH_2CH_2OH$	66	2	40	27	CH_3CH_2CHO 8, CH_3CH_2COOH	5	43	CH_3CH_2CHO 12, CH_3CH_2COOH
$(CH_3)_2CHOH$	65	2	0.5	100	$(CH_3)_2CO$ 65	3	32	$(CH_3)_2CO$ 24
$CH_3CH(OH)(CH_2)_2CH_3$	46	2	1	39	$CH_3COCH_2CH_3$ 18	1	2	$CH_3COCH_2CH_3$ 1
$[CH_3CH(OH)]_2CH_2$	23	2	15	65	$CH_3COCH_2CH(OH)CH_3$	13	0	(not detected)
cyclo-$C_6H_{11}OH$	37	2	0.6	31	cyclohexanone 11	1	10	cyclohexanone 4
$(CH_3)_3COH$	63	5	3	9	(not detected)	3	11	(not detected)
$CH_3CH_2CH_2NH_2$	65	2	2	21	CH_3CH_2CN 14	4	6	CH_3CH_2CN 4
$(CH_3)_2CHNH_2$	60	2	58	37	$(CH_3)_2CO$ 11	58	46	$(CH_3)_2CO$ 20
$(CH_3)_3CNH_2$	47	5	34	0	(not detected)	34	0	(not detected)
$[(CH_3)_2CH]_2NH$	35	5	20	42	$(CH_3)_2CO$ 11, $(CH_3)_2CHNH_2$	20	49	$(CH_3)_2CO$ 17
$(CH_3CH_2)_2NH$	48	5	37	42	CH_3CN 5	37	67	CH_3CN 14
$(CH_3CH_2)_3N$	36	5	40	47	$(CH_3CH_2)_2NH$ 10, CH_3CN 1	40	86	$(CH_3CH_2)_2NH$ 10, CH_3CN 1
$[(CH_3)_2CH]_2O$	65	5	5	90	$(CH_3)_2CO$ 50	3	0	(not detected)

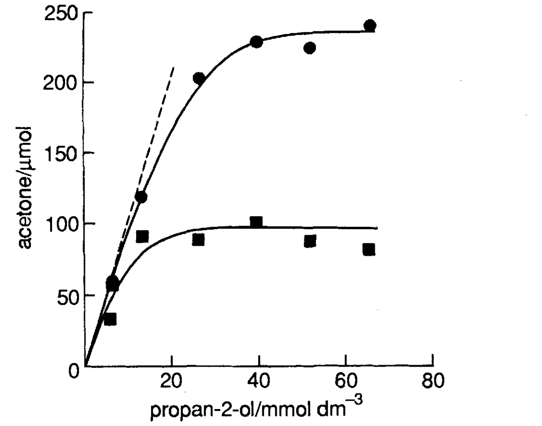

Fig. 4 Variation in acetone yield (after 10 min reaction) with the initial concentration of propan-2-ol in aqueous solution (10 cm^3) with suspended Pt (●: 20 mg and ○: 5 mg) in the presence of N_2O (0.85 mmol). Dashed line shows the quantitative conversion of propan-2-ol to acetone.

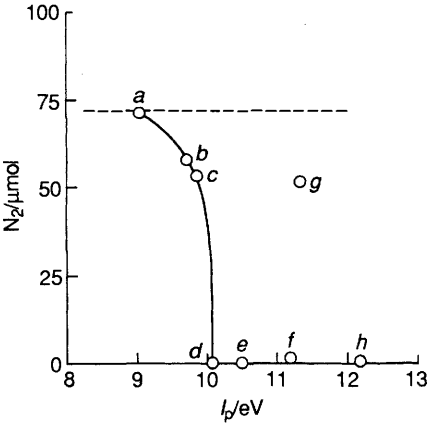

Fig. 5 Effect of additives (0.13 mmol each) on the N_2 yield in Pt (10 mg)-catalysed oxidation of propan-2-ol (0.13 mmol) with N_2O (0.85 mmol) after 5 min reaction. (*a*) 1,4-Dioxane, (*b*) acetone, (*c*) cyclohexanone, (*d*) carbon disulfide, (*e*) dibromomethane, (*f*) nitromethane, (*g*) dichloromethane, and (*h*) acetonitrile. Dashed line indicates the yield in the absence of additives.

experimental error, indicating the stoichiometry shown in eqn. (4).

$$(CH_3)_2CHOH + N_2O \longrightarrow (CH_3)_2CO + N_2 + H_2O \quad (4)$$

Palladium black (Pd) also induced the oxidation of propan-2-ol by N_2O with a lower activity (*ca.* 1/20) than that of Pt. It is noticeable that an induction period (*I*, *ca.* 45 min) was observed before N_2 and acetone formation in the Pd-catalysed oxidation under conditions similar to the Pt-catalysed reaction. Under specific conditions, the Pt-catalysed reaction also started after an induction period, as discussed later.

Fig. 4 shows the yield of acetone at a given time (10 min) of the reaction as a function of propan-2-ol concentration in aqueous solution. The yield seems to approach a finite limit, depending on the amount of Pt, with the increase of propan-2-ol concentration. A mechanism involving Langmuirian adsorption of propan-2-ol onto Pt surface can be presumed.*

A reasonable fit of time-course data to the simple first-order kinetics described below is consistent with such a mechanism, because the measurements were performed at a low concentration (13 mmol dm^{-3}) where the surface concentration is effectively proportional to the bulk concentration.

*Effect of Additives on the Catalytic Oxidation of Propan-*2-*ol*.—Fig. 5 shows the N_2 yield in the absence and presence of additives in the aqueous propan-2-ol solution; the yield was plotted, for comparison, against the ionization potential (I_p) of the additives.[20] Acetonitrile, nitromethane, dibromomethane, and carbon disulfide inhibited the propan-2-ol oxidation almost completely, while 1,4-dioxane, acetone, and cyclohexanone had a less significant effect. Thus, an appreciable inhibitory effect could be observed by the addition of compounds having I_p greater than 10 eV. An exception was dichloromethane, I_p 11.4 eV. It is unlikely that predominant oxidation of these additives, having I_p greater than propan-2-ol (10.4 eV), occurs under the present reaction conditions. In fact, negligible formation of N_2 could be observed; the oxidation of neither propan-2-ol nor additives proceeds in these experiments. Therefore, the inhibitory additives must compete, not as reductants but as

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* Quantitative evaluation of the constants for adsorption could not be achieved because of the difficulty in the precise measurement of initial rate due to the fast consumption of propan-2-ol at lower propan-2-ol concentration.

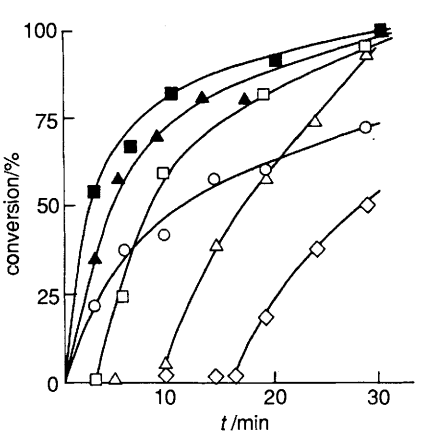

Fig. 6 Representative time-courses of Pt (5 mg)-catalysed oxidation of propan-2-ol (0.13 mmol) in buffered aqueous solutions of various pH's (○: 3, □: 7, △: 12, and ◇: 13) with N_2O. Conversion of another portion of propan-2-ol (▲) added 30 min after reaction at pH 12, and conversion of propan-2-ol (■) in the N_2O-saturated aqueous solution at pH 7 with Pt pre-treated with a H_2 stream are also plotted.

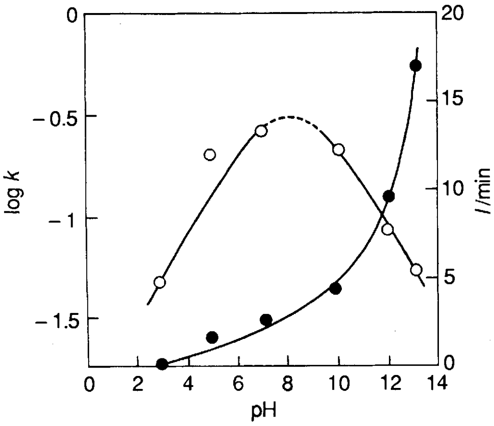

Fig. 7 Apparent rate constant (*k*; ○) and induction period (*I*; ●) in the Pt-catalysed oxidation of propan-2-ol with N_2O as a function of pH

oxidants,* with N_2O. The blocking of the surface sites for N_2O adsorption by the additives with increased electron affinity is most probable. Such an effect, poisoning the reduction sites on Pt, has been observed in the photocatalytic reaction of platinized TiO_2 suspension in acetonitrile.[21]

pH-*Dependence of Propan-2-ol Oxidation*.—Fig. 6 shows representative time courses of propan-2-ol conversion in the buffered solutions at various pH's. In the lower ($\leqslant 3$) pH region, the oxidation started just after the addition of propan-2-ol to the Pt suspension. At pH $\geqslant 5$, an induction period appeared and increased with further pH increase.†

Plots of these data showed a first-order linear relation between time and $\ln(C_0/C)$ (where C_0 and C refer to concentrations of propan-2-ol at commencement and at a given time of reaction, respectively), and values of the apparent rate constant (*k*) and induction period (*I*) were obtained for each pH as shown in Fig. 7. Maximum value of *k* was obtained at pH *ca.* 8. The absolute value of each slope of the volcano-shaped logarithmic plot in the acidic and basic regions was rather smaller than unity. This indicates that the pH dependence is not due to simple acid or base catalysis in solution but to the summation of complicated pH-sensitive processes.

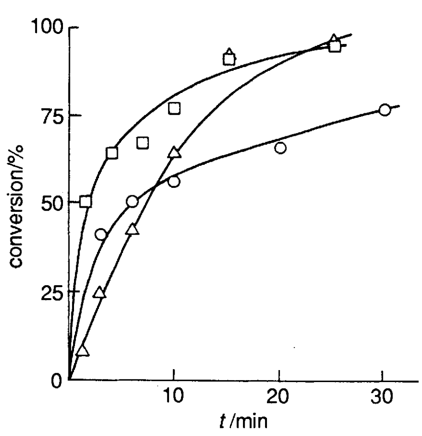

Fig. 8 Time-course of Pt (5 mg)-catalysed oxidation of propan-2-ol (0.13 mmol) in buffered solutions of various pH's (○: 3, □: 7, and △: 12) with N_2O (0.85 mmol). H_2 (0.040 mmol) was injected 30 min prior to the propan-2-ol injection.

One further finding is that even at pH 12 oxidation of another portion of propan-2-ol, added after almost complete consumption of the initial feed, proceeds without an appreciable induction period with almost the same value of *k* (Fig. 6). Therefore, a possible cause of the induction period is impurities adsorbed on the Pt surface which may readily undergo desorption or decomposition at lower pH. Fig. 6 also shows the effect of pre-treatment of the Pt suspension with H_2 at pH 7; the suspension was purged by H_2 bubbling for 30 min and then by N_2O. Clearly the induction period disappeared. The initial rate seems to be almost the same as the rate after commencement of reaction without H_2 pre-treatment. Similarly, the injection of H_2 to an N_2O-purged aqueous Pt suspension 30 min prior to the propan-2-ol injection also eliminated the induction period, without changing the order of the apparent rate of propan-2-ol oxidation (Fig. 8).

Thus, the species or moiety on the Pt surface leading to the induction period is efficiently eliminated by H_2 reduction. Species such as $O_2^{\bullet -}$ adsorbed on Pt, or partially oxidized surface sites of Pt possibly account for the H_2-induced regeneration of active sites on Pt, which adsorb N_2O with electron donation. In a similar way, electron-accepting additives such as acetonitrile should suppress the adsorption of N_2O. The markedly diminished life-time of $O_2^{\bullet -}$ in acidic media[22] can explain the pH-dependent variation of induction period shown in Fig. 7. At present, however, we have no structural evidence for such species.

Reaction Mechanism.—On the basis of the results above, the reaction mechanism in eqns. (5)–(9) is proposed. In the initial stage, the formation of radical ($^{\bullet}RH$), presumably on Pt, is required to explain the fact that the radical stabilizer HQ inhibited the reaction of DPE.

$$N_2O + Pt \longrightarrow N_2O(Pt) \qquad (5)$$

$$RH_2 \longrightarrow {}^{\bullet}RH \qquad (6)$$

$$N_2O(Pt) + {}^{\bullet}RH \longrightarrow N_2 + R + {}^{\bullet}OH(Pt) \qquad (7)$$

$$(CH_3)_2CHOH + {}^{\bullet}OH(Pt) \longrightarrow (CH_3)_2\dot{C}(OH) + H_2O \qquad (8)$$

$$N_2O(Pt) + (CH_3)_2\dot{C}(OH) \longrightarrow N_2 + (CH_3)_2CO + {}^{\bullet}OH(Pt) \qquad (9)$$

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* Although, in this respect, plots against electron affinity (E_a) may be more adequate, we used, for convenience, the more credible I_p values for these compounds.

† The reactions shown in the preceding sections were performed in non-buffered solutions. Because of the absence of supporting electrolytes, the pH of the solutions could not be measured. The solutions may be weakly acidic due to dissolved carbon dioxide and, actually, a negligible induction period was observed.

In the γ-radiolysis of aqueous propan-2-ol solution (without Pt), the G-value for N_2 evolution, *ca.* 3, was almost the same as that for e^-_{aq} (2.7),[23] indicating that N_2 was produced only by e^-_{aq}; *i.e.* the reductive decomposition of N_2O* by the 2-hydroxy-2-propyl radical (2HP) was negligible in aqueous solution. However, on the assumption of electron donation from Pt to the adsorbed N_2O, N–O bond cleavage by 2HP (oxidation potential in aqueous solution has been reported as *ca.* -1 V *vs.* NHE)[24] should be feasible. The resulting $^{\bullet}OH$ radical abstracts hydrogen from the substrate, propan-2-ol, to yield 2HP predominantly[13] as a carrier of this chain reaction sequence. The chain breaking reactions, *e.g.* disproportionation [eqn. (10)] or recombination [eqn. (11)] of these radicals are also feasible.

$$2(CH_3)_2\dot{C}(OH) \longrightarrow (CH_3)_2CHOH + (CH_3)_2CO \quad (10)$$

$$(CH_3)_2\dot{C}(OH) + {}^{\bullet}OH(Pt) \longrightarrow [(CH_3)_2C(OH)_2] \longrightarrow (CH_3)_2CO + H_2O \quad (11)$$

In this mechanism rate for acetone production (*i.e.* N_2 evolution) is proportional to the surface concentration of N_2O, provided that reaction (8) proceeds readily, as in the homogeneous system,[13] and, therefore, reduction of N_2O by 2HP [reaction (9)] is the rate determining step.†

In practice, the initial rate increased with the increasing amount of Pt (data not shown). On the other hand, the term including propan-2-ol concentration in the rate expression depends strongly on the initiation and termination reactions. The apparent first-order dependence may be expected.

The higher reactivity of propan-2-ol is explained by the higher reducing ability of the corresponding radical, 2HP, since its reactivity in reaction (9) may determine the overall reaction rate. Among α-hydroxyalkyl radicals from simple aliphatic alcohols, 2HP shows the highest reduction ability.[25] DPE may produce the same radical *via* the reaction (12).

$$[(CH_3)_2CH]_2O + {}^{\bullet}OH \longrightarrow (CH_3)_2\dot{C}(OH) + (CH_3)_2CHOH \quad (12)$$

The dissociation constant (pK_a) of the proposed active species, $^{\bullet}OH(Pt)$, is unknown. The pH-dependence of rate constant for propan-2-ol oxidation is partly attributable to the difference in reactivity between deprotonated and protonated forms of $^{\bullet}OH(Pt)$.

Conclusion

Platinum-catalysed oxidation or oxidative decomposition of various organic compounds proceeds at room temperature, accompanied by the decomposition of N_2O to give N_2. From detailed studies on the characteristic induction period observed before commencement of the catalytic reaction, and on the inhibiting effect of additives, a reaction mechanism involving reductive adsorption of N_2O by Pt and chain reaction with radical intermediates is proposed. The higher reactivity of propan-2-ol in the catalytic oxidation is attributed to the greater reducing ability of 2-hydroxy-2-propyl radical.

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* A polarographic study has revealed that the reduction potential of N_2O dissolved in a weakly acidic solution is more negative than -1.6 V *vs.* NHE.[15]

† Application of the steady state approximation for the radicals to this reaction sequence allows us to predict the rate being proportional to the surface concentration of N_2O.

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