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Hydrogenation of Nitroxides on Pt/SiO_2

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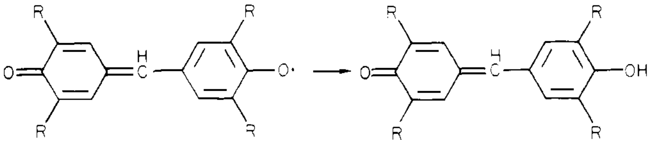
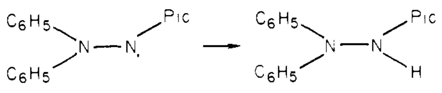
Abstract: The hydrogenation of the nitroxide 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TMPNO) in ethylcyclohexane and other solvents has been studied from 0.6 to 35 °C on Pt/SiO_2. Hydrogenations were sandwiched between hydrogenations of cyclopentene using the techniques of Hussey et al.[11] Results were shown to be uninfluenced by mass transfer of hydrogen between gas and liquid phases and in the catalyst pores. Significant levels of poisons in the TMPNO appeared to have been absent. Rates of hydrogenation of TMPNO to the hydroxylamine were very fast. At 20 °C, turnover frequencies per second per surface atom of Pt for the loss of unsaturated molecules were ~130 for TMPNO and ~13 for cyclopentene, and E_a's were 21 and 34 kJ mol^{-1}, respectively. The rates were zero order in TMPNO and about first order in hydrogen. In competitive hydrogenations of equimolar mixtures, TMPNO hydrogenated 3 times faster than cyclopentene. It appears that both TMPNO and cyclopentene adsorb strongly enough on Pt to form an essentially saturated adsorbed layer and that the rate of hydrogenation is that of the dissociative adsorption of hydrogen at gaps in the adsorbed layer of the unsaturated molecule. The relative rates of hydrogenation of such molecules are then proportional to the product (effective area of gaps) × (sticking coefficient of hydrogen).

Many studies have dealt with the addition of *two* hydrogen atoms to such unsaturated molecules as alkenes and ketones, and there has been extensive mechanistic discussion regarding such hydrogenations. On the other hand, few papers have considered hydrogenations in which only one *atom*[3] of hydrogen adds to an unsaturated molecule, that is, to a free radical.

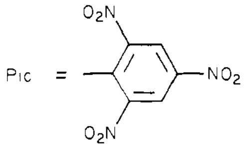
An early example of such a hydrogenation was given by Coppinger,[4] who reported the hydrogenation on platinum of the resonance-stabilized free radical I (where R is *tert*-butyl) to II followed by addition of H_2 to the group at the left of II. The first more detailed study of the hydrogenation of a free radical was that of Balandin et al.[5] This work involved the hydrogenation of 1,1-diphenylpicrylhydrazyl (III) on Rh/Al_2O_3 in aqueous acetic acid at 20–25 °C. The reaction was slow, but since the rate was nearly independent of the amount of catalyst, agitation must have been poor, and the observed rate was essentially that of transfer of H_2 from the gas to the solution phase.[6]



I II



III IV



The discovery of the air-stable nitroxide free radicals by Hoffman and Henderson[7] provided a simpler and more stable type of free radical for study, and in their first publication[7] these authors noted that the nitroxide was readily hydrogenated on platinum to the hydroxylamine. A number of similar preparative hydrogenations of nitroxides have been reported by Rozantsev.[8] All involved nitroxides with tertiary carbon atoms adjacent to the nitrogen atom since nitroxides with primary or secondary groups in this position are unstable.

$$\underset{\text{V}}{(t\text{-Bu})_2\text{N}\overset{\cdot}{-}\text{O}} + {}^1\!/_2\text{H}_2 \rightarrow \underset{\text{VI}}{(t\text{-Bu})_2\text{N-OH}}$$

Several years ago in this laboratory,[9] we studied the hydrogenation of V adsorbed from the vapor phase onto Pt/SiO_2 and

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(3) *Atom* and not a hydride ion or a proton. We exclude addition of protons to carbanions and the heterogeneous hydrogenation of carbonium ions such as $(C_6H_5)_3C^+ + H_2 \rightarrow (C_6H_5)_3CH + H^+$ on Pt/C. See: Wristers, J. *J. Chem. Soc., Chem. Commun.* **1977**, 575–576.

(4) Coppinger, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 501–502.

(5) Balandin, A. A.; Khidekel, M. L.; Patrikeev, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1959**, 361–362.

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Pt/Al_2O_3. The reaction was so fast that it had to be studied at −70 °C. The measured rate appeared to be that of migration of V on the surface of the oxide support to the platinum crystallites. It also appeared that the reaction[10]

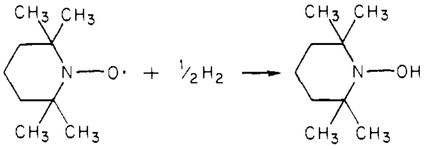
$$R_2N\dot{-}O + HONR_2 \rightarrow R_2NOH + O\dot{-}NR_2 \qquad (1)$$

was fast in the adsorbed phase. This investigation provided little information bearing on the mechanism of the actual hydrogenation step, but one could be curious as to whether it proceeded by analogy to eq 1 as a simple abstraction process,

$$R_2NO\cdot + H^* \rightarrow R_2NOH + {}^* \qquad (2)$$

without preliminary adsorption of $R_2NO\cdot$ or whether the mechanism involved preliminary adsorption of R_2NO.

The work reported in the present paper involves a study of the hydrogenation of solutions of 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TMPNO) (VII) on Pt/SiO_2 catalysts. Such studies are subject to substantial difficulties. (1) One must ensure that agitation is adequate to maintain equilibrium between gas phase and dissolved hydrogen, otherwise the observed rate depends mainly on the rate of transfer of hydrogen from the gas to the solution. (2) One needs to ensure that significant concentration gradients of hydrogen in the catalyst pores are absent; otherwise transport of hydrogen in the pores complicates the kinetics. (3) One must demonstrate that the measured rate is free from the effect of poisons. Only a handful of papers on hydrogenations in the liquid phase have made any attempt to demonstrate that all of these conditions were satisfied. Indeed, few of them have considered any of these problems. Avoidance of significant poisoning is usually not trivial. Thus, if one molecule of poison blocked several surface sites and if one uses 10 mg of 0.2% Pt/SiO_2 with a percentage exposed of Pt of 60% (6×10^{-8} mol of surface atoms of Pt), 0.1 ppm of a strong poison in 0.01 mol of solvent could block $\sim 10^{-8}$ mol of surface platinum atoms, Pt_s, and significantly affect rates. Significant poisoning has probably been present in most studies of catalytic hydrogenation in the liquid phase. In purely preparative work, this may be of little consequence, but it is serious in attempted studies of the hydrogenation process.



TMPNO TMPNOH

In the present work we planned to employ the procedure originally developed by Hussey[11] and later employed by us.[12] In a number of solvents where conditions 1, 2, and 3 are satisfied, the hydrogenation of cyclopentene on Pt is strictly zero order in olefin down to very low concentrations of olefin. One first injects cyclopentene into the reactor and records its hydrogenation. Some other compound is then injected and its hydrogenation recorded. Cyclopentene is again injected and hydrogenated. If the rate of consumption of hydrogen is independent of time and is the same in both injections 1 and 3, then the system has probably been free of poisons throughout.

To test for satisfying condition 1, one measures the rate of hydrogenation as a function of the amount of catalyst.[6,12] The system is free of the effects of transport of hydrogen from the gas to the liquid phase for amounts of catalyst from zero to the end of the range in which rate is linear with amount of catalyst. Condition 2 is satisfied for catalysts with granule sizes smaller than the size at which rate no longer increases with decreasing granule size. Conditions 1 and 2 were satisfied in the work reported here, but, as will be seen, problems arose with respect to condition 3.

Experimental Section

Reagents and Materials. Hydrocarbons were refluxed over potassium, distilled thence in nitrogen, and stored under nitrogen in a flask provided with a Teflon needle valve by means of which hydrocarbon could be removed without exposure of the main mass of hydrocarbon to air.[12] Ethylcyclohexane was passed through a column of Davison Grade 952 silica gel before refluxing with potassium. Lower boiling hydrocarbons like cyclopentene were refluxed under pressure to melt the potassium. *tert*-Butyl and *tert*-amyl alcohols were purified by distillation followed by repeated fractional crystallization.

Tetramethylpiperidine (TMP) (Aldrich Chemical Co.) was distilled from solid KOH; the main fraction, bp 153.5–154 °C (lit. 155.5–156 °C), was used. This was converted into tetramethylpiperidinyl-*N*-oxy (TMPNO) by the method of Brière et al.[13] A solution of TMP (1.0), H_2O (10), 30% H_2O_2 (2.0), and phosphotungstic acid (0.01) (the numbers are the relative masses of the reagents) was stirred for 2–3 days, TMPNO was extracted with ether and the ether washed 6 times with 0.5 M H_2SO_4 to remove unreacted TMP and then with water. After the solution was dried over Drierite, the ether was evaporated at 25 °C in a rotary evaporator. The residue was purified by sublimation, and usually twice sublimed material was used in catalytic experiments, mp 39.3–39.8 °C.

All Pt/SiO_2 catalysts were made by ion exchange of silica gel with $Pt(NH_3)_4^{2+}$.[14] Most of the work employed a 0.224 wt % Pt on Davison Grade 952 silica gel in which an ion-exchange period of 4 h was employed. It is designated 0.2-Pt-952, and it was used unless otherwise specified. Grade 952 is a wide-pore gel with an average pore diameter of 20 nm, a pore volume of 1.65 $cm^3\ g^{-1}$, and a specific surface area of about 300 $m^2\ g^{-1}$. As measured by the chemisorption of hydrogen at 25 °C,[14] the percentage exposed of platinum, D_h, was 72%. A 0.234 wt % Pt on 230–400 mesh Davison Grade 62 was also prepared, 0.2-Pt-62.

The γ-alumina diluent was Aero 1000 of the American Cyanamid Co., 200–230 mesh, calcined in air at 540 °C, rehydrated over water for 78 h at 25 °C, and dried in an oven at 200 °C. It had zero activity for hydrogenation of TMPNO and cyclopentene.

Techniques. The apparatus and general procedures have been described.[12] A small reactor was agitated by rotation about a circle of a radius of 3 mm, and it was connected to a thermostated bulb usually 2 L in volume. The reaction solution plus catalyst was converted nearly to an aerosol during agitation. The fall in pressure during reaction was recorded from the output of a capacitance manometer. Since pressure falls were less than 1% of the total pressure, the system had the advantages of both a constant volume and a constant pressure system.

Hydrogen was provided by an Elhygen (Milton Roy) electrolytic generator in which the hydrogen passes through a Pd,Ag wall. Total pressures were ~750 torr unless otherwise stated. The actual pressure of H_2 was calculated by subtracting the vapor pressure of the solvent from the total pressure.

Since the nitroxide is solid at 25 °C, it was injected (injection 2) as a solution in 0.5 cm^3 of the solvent to be employed, and usually ~0.7 mmol of TMPNO was used. The quantity of catalyst was usually ~10 mg, and the amount of solvent initially injected was 1.0 cm^3. In addition, ~100 mg of alumina was added initially to the reactor, since if this was not done the catalyst tended to stick to the walls of the reactor and rates of hydrogenation would decline somewhat with time. The amount of cyclopentene injected in injections 1 and 3 was usually 0.68 mmol. To ensure that cyclopentene and solvent were free of poisons, we required that several successive injections of cyclopentene should all lead to the same rate independent of time to above 99% conversion.

An initial problem was the choice of solvent. We knew from previous work that several alkanes could satisfy the requirement just given, but in preliminary experiments using di-*tert*-butyl nitroxide, Donald Barry had found that the hydroxylamine precipitated during hydrogenation in alkanes. He also found that precipitation did not occur in *tert*-butyl alcohol and that the solvent purified by successive fractional crystallizations satisfied the purity requirement. The suitability of *tert*-butyl alcohol was confirmed in the present work. However, since the vapor pressure of the alcohol is rather large, its vapor pressure in the reactor reduces P_{H_2} and complicates the evaluation of the actual P_{H_2}. Further, its high mp, 25.5 °C, prevents one from running hydrogenations at lower temperatures. Ideally, one should employ a solvent with a melting point

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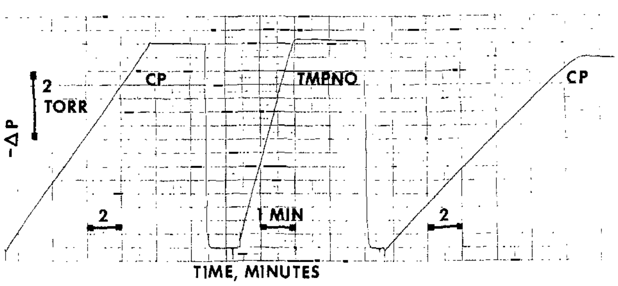

Figure 1. Hydrogenation at 25 °C of three successive injections on 10.0 mg of 0.2-Pt-952; from left to right (1) cyclopentene, (2) TMPNO (1.5 mmol), (3) cyclopentene. The vertical axis is $-\Delta P$(hydrogen); the horizontal axis is time in minutes with unit time for TMPNO being twice as long as that for cyclopentene.

below 0 °C and with a boiling point as high as possible. *tert*-Amyl alcohol (mp, -8.4 °C) offered promise, but it did not satisfy the purity requirement even after six successive crystallizations plus refluxing over CaO or passage through a column of alumina. We then found that TMPNO, unlike VI, did not precipitate from alkanes or cycloalkanes. Heptane, octane, cyclohexane, methylcyclohexane, and ethylcyclohexane all satisfied the purity requirements, although in some cases refluxing with and distillation from potassium had to be repeated. Most of the work reported here employed ethylcyclohexane (Matheson, Coleman, and Bell) (bp 131.8 °C; vapor pressure at 20.5 °C, 10 torr).

The stored catalyst was exposed to air after preparation and became covered with adsorbed oxygen.[14] It was exposed to hydrogen in the reactor, the hydrogen was evacuated and then readmitted, solvent was injected, and the system was agitated for 15 min. Cyclopentene was then injected and hydrogenation started. One might worry that removal of oxygen from the platinum was incomplete. However, using a temperature of 100 °C rather than 25 °C during the 15-min initial exposure to hydrogen led to little difference in the rate of hydrogenation.

In runs at 0-35 °C, the rate of hydrogenation of cyclopentene was nearly independent of time, as exemplified by injection 1 in Figure 1. Several successive injections of cyclopentene led to identical results. When TMPNO was used in injection 2, the course of hydrogenation was like that shown in Figure 1. ΔP vs. time was linear to beyond 90% conversion, and the rate of consumption of hydrogen was about 5 times as fast as with cyclopentene, but near 100% conversion, the rate declined more gradually than with cyclopentene. Injection 3 (cyclopentene) then exhibited an initial rate of 83 ± 3% that of injection 1 when 0.7 mmol of TMPNO had been used in injection 2, and the rate declined slowly with increasing conversion as shown in Figure 1. Another injection of cyclopentene led to a still lower initial rate and a greater degree of decline. These phenomena were exhibited by runs at 0-35 °C in ethylcyclohexane and in runs at 20-25 °C in heptane, octane, cyclohexane, methylcyclohexane, *tert*-butyl alcohol, and mixtures of heptane and *tert*-butyl alcohol. Increased quantities of TMPNO in injection 2 led rate 3/rate 1 to decrease. Thus, in Figure 1, rate 3/rate 1 was 0.76, and a further injection of cyclopentene gave 0.62. However, the initial rate of hydrogenation of TMPNO was independent of the amount of TMPNO in the range 0.5-1.5 mmol. Comparison of the recordings for injection 3 with that for injection 1 shows that some weak poison either was present in TMPNO initially or was generated during its hydrogenation. In addition, the further decreased rate resulting from an additional injection of cyclopentene suggests that some poison was formed by interaction between cyclopentene and TMPNOH.

Subliming the crude TMPNO led the rate of hydrogenation to triple. Successive resublimations had negligible effect. Further, recrystallization of TMPNO from heptane or ether before sublimation made no change. If injection 1 was TMPNO, the course of hydrogenation of TMPNO in injections 1 and 2 was the same and the same as when injection 1 was cyclopentene. The terminal decline in the rate of hydrogenation of TMPNO might have been thought to originate from strong adsorption of some TMPNO on the alumina diluent, but replacement of the alumina by 150+ mesh glass beads led to no change in the general course of the hydrogenation.

Since some TMP might have been generated during hydrogenation by hydrogenolysis, some runs were made in which TMP was added to TMPNO. In a run with 0.50 mmol of TMPNO and 0.16 mmol of TMP, the rate of hydrogenation was 70% that of TMPNO alone, but the nature of the terminal decline of rate with time was little affected. Since we were unsuccessful in analyzing the product of hydrogenation of TMPNO by gas chromatography (TMPNOH appeared to decompose in the injection region), we filtered the product of hydrogenation from the catalyst and then evaporated the solvent, all with the exclusion of air. The melting point of the residue was measured in a sealed capillary, mp 38.5-40.2 °C vs. the literature report for TMPNOH, 39-40 °C.[15] If impurities in TMPNOH are insoluble in the solid, their amount could not have exceeded a few percent. We conclude, then, that formation of TMP is not a significant contributor to declines in rates.

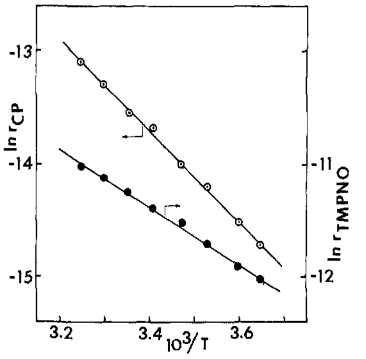

Figure 2. Rates of hydrogenation of cyclopentene and of TMPNO in mol s^{-1} on 10 mg of 0.2-Pt-952 in ethylcyclohexane as solvent as a function of temperature. *y* axis at left, ln (rate of loss of cyclopentene); at right, ln (rate of loss of TMPNO); *x* axis, 1000/*T*.

Table I. Rates of Hydrogenation on 0.2-Pt-952 at 20 °C in Several Solvents

solvent	r_{cp}[a]	r_{TMPNO}[b]	r_{TMPNO}/r_{cp}
cyclohexane	1.15	11.8	10.3
ethylcyclohexane	1.16	11.9	10.3
methylcyclohexane	1.09	9.7	9.0
heptane	1.36	17.3	12.7

[a] Rate of loss of cyclopentene in μmol s^{-1} (10 mg of catalyst)$^{-1}$.
[b] Rate of loss of TMPNO in μmol s^{-1} (10 mg of catalyst)$^{-1}$.

It appears likely that TMPNOH is a weak inhibitor for hydrogenation of both TMPNO and cyclopentene, but we have not rigorously excluded the presence of some inhibitor in the TMPNO. It also appears likely that some poison is formed by reaction between TMPNOH and cyclopentene.

As the following experiments demonstrate, the terminal decline in rate during hydrogenation of TMPNO is not some artifact of mass transfer. This question needed attention because of the very fast hydrogenation of TMPNO. Runs were made in which the amount of 0.2-Pt-952 was varied from 6.2 to 28.3 mg. The initial rate for cyclopentene was proportional to the amount of catalyst over the entire range, but with TMPNO the rate fell below the linear plot beyond 15 mg. Thus, H_2 in solution and H_2(g) were essentially in equilibrium when 10 mg of catalyst was employed. Runs were made with 0.2-Pt-952 of 80-140, 200-230, 230-400, and 400+ mesh. Grade 952 silica gel was ground and sieved to the meshes given above and washed, as usual, with redistilled water, 0.1 M HNO_3, and water. Portions of the different mesh sizes were mixed, and the mixture was subjected to ion exchange with $Pt(NH_3)_4^{2+}$ and processed in the usual way. The final catalyst after reduction was resieved into the specified mesh sizes. The 230-400 portion was the standard 0.2-Pt-952 catalyst. The same rates were obtained with 230-400 and 400+ mesh catalyst; 200-230 gave 84% of this rate for TMPNO and 95% for cyclopentene; and 80-140 gave 52% and 73%, respectively. Thus, concentration gradients of hydrogen in the pores of 230-400 mesh should have had a negligible effect on rates.

Kinetic order in hydrogen was measured approximately at 20 and 5 °C with P_{H_2} varying from 0.86 to 1.3 atm. In this range the kinetic order in hydrogen was 1 ± 0.2 for the hydrogenations of both TMPNO and cyclopentene. The pressure range available with our apparatus was too low to permit precise measurement of the kinetic order of hydrogen, but it was adequate to show that the kinetic order was near unity.

The rates of hydrogenation were measured from 0.6 to 35 °C in intervals of 5 °C. As shown in Figure 2, graphs of ln r vs. $1/T$ were linear to within experimental error. E_a was 21 kJ mol^{-1} for TMPNO and 34 kJ mol^{-1} for cyclopentene.

Rates of hydrogenation on 0.2-Pt-952 are shown in Table I. r_{TMPNO}/r_{cp} is in terms of disappearance of unsaturate. The ratio of the rates of consumption of hydrogen is one-half as large. The usual reproducibility in rates was ±5%. Rates for methylcyclohexane may be

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[15] Rozantsev, E. G.; Gurianova, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 979-983.

low since this solvent was difficult to free of poisons. In *tert*-butyl alcohol/heptane = 1.49 at 25 °C, 0.2-Pt-952 and 0.2-Pt-62 gave nearly the same rates, 77% of that in ethylcyclohexane, and r_{TMPNO}/r_{cp} was 7.6. In this mixed solvent, 0.5-Pt-62 (63.5-SiO_2-IonX of ref 14, crushed and sieved to 200–400 mesh) hydrogenated cyclopentene 2.4 times as fast as did 0.2-Pt-62.

Competitive Hydrogenations. Hydrogenations of mixtures of cyclopentene and TMPNO (as injection 2) were sandwiched between runs with pure cyclopentene (injections 1 and 3). The value of r_3/r_1 was always less than the 0.83 ± 0.03 observed when injection 2 was TMPNO alone. When TMPNO/C_5H_{10} was 5.0, r_3/r_1 was 0.62, when TMPNO/C_5H_{10} was 1.0, r_3/r_1 was 0.5, and when TMPNO/C_5H_{10} was 0.17, r_3/r_1 was ~0.65.

If one takes the rate of consumption of H_2 in injection 1 (cyclopentene) as unity, the rate of consumption of H_2 by TMPNO alone would be 5.1. When TMPNO/C_5H_{10} was 1.0 and 0.17, the recording of H_2 consumed vs. time consisted of two nearly linear sections joined by a curved section. In the first case, the relative slope of the first section was 1.29 and that of the second section was 0.68. In the second case, the values were 1.11 and 0.81. At TMPNO/C_5H_{10} = 5.0, the recording consisted of an initial linear section of relative slope = 1.76 followed by a section of steadily decreasing slope.

In other runs, samples were removed at various times and analyzed for cyclopentene and cyclopentane by gas chromatography. The amounts of TMPNO and TMPNOH present at each point were calculated from the amount of cyclopentene formed and the hydrogen consumption. When $(TMPNO)_0/(C_5H_{10})_0$ was 1.0, initially about 3 times as much TMPNOH was formed as cyclopentane.

Attempts were made to study the competitive hydrogenation of 3-hexyne and TMPNO. The actual rate of hydrogenation was very much less than that of TMPNO alone. However, we had difficulties in purifying 3-hexyne, and results are of dubious reliability.

Discussion

As has been shown, the rates of hydrogenation of TMPNO and cyclopentene reported in this paper are free from influences of mass transport of hydrogen in the catalyst pores and between the gas and liquid phases. The hydrogenation of cyclopentene alone appears to have been uninfluenced by poisoning, since the rate of hydrogenation was constant to beyond a conversion of 99.5% and no decline in rate ws observed with successive injection. At 20 °C in ethylcyclohexane and cyclohexane, the turnover frequency N_t was about 13 s^{-1} per Pt_s. In previous work using a number of different Pt/SiO_2 prepared by ion exchange (but none on Grade 952), values of N_t varied from 8.3 to 15.7 s^{-1}.[12]

The hydrogenation of TMPNO was very fast (Table I). At 20 °C the rate of disappearance of TMPNO was about 10 times faster than that of cyclopentene; i.e., the rate of consumption of hydrogen was 5 times faster. As far as we are aware, the hydrogenationation of TMPNO is the fastest of any substance so far reported in the liquid phase on platinum at 25 °C. As shown in Figure 1, the rate of hydrogenation was constant to ~95% reaction, following which the rate dropped substantially. Conceivably, the decline resulted from the concentration gradient of TMPNO in the catalyst pores becoming serious relative to the concentration at low concentrations of TMPNO. However, the nature of the downward curvature was not detectably different at 0.6 and 35 °C although the rates varied by a factor of 2.6. Further, it was little affected by variation in the granule size of the catalyst.

The hydrogenation of cyclopentene in injection 3 (after TMPNO) was somewhat poisoned. The initial rate was 0.83 ± 0.03 that of injection 1, and the rate declined with conversion. The initial rate in injection 3 was smaller when larger quantities of TMPNO had been used in injection 2. The initial rate was still smaller when injection 2 consisted of mixtures of TMPNO and cyclopentene. Further, when TMPNO alone had constituted injection 2, an injection of cyclopentene following injection 3 led to still smaller initial rates of hydrogenation. Attempts at further purification of TMPNO beyond that effected by two sublimations led to no change in the course of the hydrogenation of injections 2 and 3. Initial rates of hydrogenation of TMPNO were the same when the amount of TMPNO injected was varied from 0.5 to 1.5 mmol, and the hydrogenation of a second injection of TMPNO exhibited the same rate as the first injection. The presence of any TMP in TMPNO or the formation of TMP by the hydrogenolysis of TMPNO during its hydrogenation did not contribute significantly either to the final departure from zero order during the hydrogenation of injection 2 or to the poisoning in injection 3. Further, as judged by the melting point of the product of hydrogenation of TMPNO, the hydrogenation leads to TMPNOH of rather high purity. Although we have not rigorously established the absence of poisons in TMPNO, we think that the final decline from zero order during hydrogenation of TMPNO and the poisoning in injection 3 results from TMPNOH acting as a rather weak competitive inhibitor and from some poison being formed by reaction between cyclopentene and TMPNOH.

Thus, although there is some uncertainty as to the origin of the poisoning manifested in the hydrogenation of cyclopentene in injection 3, we think that injection 1 is free of poisons and the hydrogenation of TMPNO is free of the effects of poisoning to at least ~95% conversion.

Mechanism. If the hydrogenation of TMPNO occurred by eq 2, that is, by direct H-atom abstraction by unadsorbed TMPNO, if a power rate law, $r \propto P_{TMPNO}{}^{n}P_{H}{}^{m}$, can be applied, and if the rate constants of the steps are such that coverages by TMPNO and TMPNOH are very low, n would be unity since the rate of eq 2 would be proportional to [TMPNO]. The value of m might be zero if coverage by H_2 is near unity, $^1/_2$ if coverage by dissociatively adsorbed hydrogen is low but in preequilibrium, or unity if coverage is small and irreversible. None of these possibilities accords with the observed values, $n = 0$, $m = 1$.

In the hydrogenation of cyclopentene on Pt, the adsorptions of both olefin and hydrogen are nearly irreversible[16] and $n = 0$, $m = 1$; i.e., there is no preequilibrium step and, therefore, no rate-limiting process. It was proposed[16] that the surface of the platinum is covered by an essentially saturated monolayer of adsorbed cyclopentene and cyclopentyl, that hydrogen adsorbs dissociatively and irreversibly at gaps in the layer of adsorbed hydrocarbon, and that reaction of *H is fast so that its coverage is low and the rate of reaction is proportional to the rate at which H_2 strikes the gaps. A similar model can account for the kinetics observed in the hydrogenation of TMPNO.

$$H_2 + 2{*} \rightarrow 2H{*} \qquad (3)$$

$$TMPNO + {*} \rightarrow TMPNO{*} \qquad (4)$$

$$H{*} + TMPNO{*} \rightarrow 2{*} + TMPNOH \qquad (5)$$

Presumably, reaction 5 occurs in two steps: first, formation of adsorbed hydroxylamine $R_2N(H)O*$; second, desorption of hydroxylamine. Adsorption of hydrogen (reaction 3) must be followed by reaction 5 and desorption within a few milliseconds or less or else the platinum at the gaps would become covered by hydrogen and the kinetic order in hydrogen would fall below unity. That is, the rate *constants* for both steps of reaction 5 are so large that the actual values do not influence the rate of hydrogenation.

If the rate of reaction 4 was not large enough to make the coverage by TMPNO (or hydrocarbon in the hydrogenation of olefins) essentially independent of the concentration of TMPNO (or olefin), the overall rate of hydrogenation would increase at lower concentrations of TMPNO (or olefin) and the reaction would not be exactly zero order in unsaturate. That is, coverage by unsaturate would fall at lower concentrations and the area available to hydrogen would rise. In fact, since there usually appeared to be a slight increase in the rate of hydrogenation of cyclopentene toward the end of its hydrogenation, this situation may apply in these hydrogenations to a slight extent.

Reaction 2 may occur for one cycle when nitroxide is first added to H-covered Pt, and it might be thought that reaction 2 would compete with reaction 5 throughout the hydrogenation. However, if adsorption of TMPNO, reaction 4, is slow at the gaps in the surface layer, one would also expect reaction 2 to be slow. Thus, we conclude that the hydrogenation of TMPNO proceeds mainly by the sequence, reactions 3, 4, 5.

On this model, the relative rate of hydrogenation per unit area of metal surface is proportional to W, the product of the number

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[16] Kung, H. H.; Burwell, R. L., Jr. *J. Catal.* **1980**, *62*, 11–24. See also ref 11 with respect to the irreversible adsorption of olefin.

of sites per unit area available to hydrogen (i.e., to the effective area of the gaps in the packing of the adsorbed unsaturated molecules) times the sticking coefficient of hydrogen at those gaps. If the olefin (or other unsaturated molecule) is so strongly adsorbed as to lead to rates that are zero order in olefin, then the relative rates of hydrogenation of various olefins depend only upon the relative values of the product *W*. In competitive hydrogenations, the ratio of the rates of hydrogenation would depend upon the relative rates of adsorption of the two unsaturated molecules in reactions equivalent to (4). In competitive hydrogenations of olefins, cyclopentene is one of the best competitors,[11] but TMPNO is even better, and the ratio of the rates of adsorption of TMPNO and cyclopentene is ~ 3.

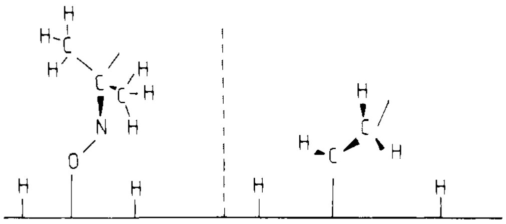
A study of the hydrogenation of TMPNO with RC≡C— and RHC=CH— substituted in the 4-position on the ring has been reported.[17] On platinum, the nitroxide function was hydrogenated preferentially, but on palladium, the acetylenic and olefinic functions were hydrogenated preferentially. The same authors[18] also reported a study of the hydrogenation of molecules consisting of two TMPNO residues joined at the 4-positions via a $-O_2C(CH_2)_8CO_2-$ or a $-O_2C(CH_2)_{12}CO_2-$ chain. They reported that the initial product was the monohydroxylamine, none of which was further reduced until all biradical had disappeared. However, they did not consider the possibility of the occurrence of reaction 1.

The ΔH_{ads} of the unsaturated molecule should influence selectivity in competitive hydrogenations with the molecule with the larger negative ΔH_{ads} adsorbing faster in reaction 4. ΔH_{ads} should, however, have no direct influence on the absolute rate of hydrogenation, which depends only upon the rate of adsorption of hydrogen at the gaps, provided of course that adsorption of unsaturate is sufficiently strong. This is usually the case, but for example, the highly hindered *trans*-di-*tert*-butylethylene is an exception.[12] The usual increase in rate, which occurs during the hydrogenation of a substituted acetylene after all acetylene has been converted to olefin, would be ascribed primarily to better packing in the adsorbed layer of acetylene than in that of olefin. The area occupied by an adsorbed, unsaturated molecule would not of itself influence the rate of hydrogenation[19] unless the sticking coefficient of hydrogen was influenced by the number of bonded >C=C< groups per unit area.

On our model, TMPNO hydrogenated more rapidly than cyclopentene because of a larger value of *W*. Unfortunately, we have no rigorous way of independently evaluating the two terms in *W*. Adsorption of an unsaturated molecule will block adsorption of other such molecules at a number of platinum atoms adjacent to the one or ones actually involved in binding the unsaturated molecule. Adsorption of H_2 may still be possible at some of these atoms. In general the number of such sites available to hydrogen will vary with the nature of the adsorbed molecule. Presumably, the sticking coefficient of hydrogen will be influenced electronically by the adsorption of unsaturated molecules at neighboring sites, but we can say nothing quantitative about this.

The very rapid rate of hydrogenation of TMPNO implies that its packing density is lower than that of olefins. However, the resulting effective area for the adsorption of hydrogen may, at least in part, result from difference in the nature of adsorbed nitroxides and adsorbed olefins. In particular, the bulky part of the nitroxide will stand much farther from the surface than in the case of olefins, and atoms of hydrogen may be able to adsorb under some of the bulky parts of nitroxide as shown in Scheme I. In this, one is looking parallel to the ring of TMPNO and through the two carbon atoms of the double bond of the olefin. Equivalent sets of C and H atoms are obscured behind those shown. The ring of the nitroxide is assumed to be in a chair conformation. Further, because of the structure of adsorbed nitroxide, nitroxide might be able to adsorb at relatively small gaps in the adsorbed layer. This might help to explain the competitive effectiveness of the nitroxide. In general, in competition, a molecule of low packing area might win over a more strongly adsorbed but more bulky molecule.

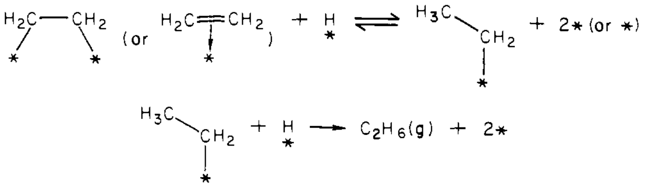
Scheme I



In competitive hydrogenations of equimolar mixtures of cyclopentene and TMPNO, the initial product is 0.75 TMPNOH and 0.25 cyclopentene. Since the rate of consumption of hydrogen by TMPNO when alone is 5.1 times that of cyclopentene, one might expect the initial rate of hydrogenation of the mixture relative to that of cyclopentene alone to be 0.75 (5.1) + 0.25 (1.0) = 4.08. In fact, the observed initial relative rate was only 32% of 4.08. It seems likely that the sticking coefficient of hydrogen in the competitive case would be intermediate between the values for the two compounds alone. If so, then the depressed rate in the competitive runs would be ascribed to packing being tighter in the competitive runs than in runs with either pure compound. For this reason, we think that in practice variation in *W* is likely to be due mainly to variations in packing density.

On the model, temperature will affect the rate of hydrogenation by its effect upon *W* and upon the concentration of H_2 in the solvent. The latter effect should be the same for all unsaturated compounds, and it makes a positive contribution to E_a since the solution of hydrogen in these solvents is endothermic; i.e., its solubility increases with increasing temperature. Since E_a for cyclopentene is larger than that for TMPNO, dW/dT is larger, but we cannot say securely whether the free area or the sticking coefficient changes more rapidly with temperature.

We conclude, then, that nitroxides are hydrogenated much like olefins. That is, adsorption of nitroxides is so rapid and strong as to lead to an essentially saturated adsorbed layer, and the overall rate of hydrogenation is the rate of adsorption of hydrogen at gaps in the adsorbed layer. In competition, the rate of adsorption of nitroxide is equal to that of the best competing olefins. Furthermore, the hydrogenation of a nitroxide is the simplest example of a hydrogenation, since reaction of >NO* with H* involves only one surface step, whereas hydrogenation of olefins involves two steps. For example, in the simplest case, the two steps are



$$\underset{*}{H_2C}-\underset{*}{CH_2}\ (\text{or}\ \underset{*}{H_2C{=}CH_2}) + \underset{*}{H} \rightleftharpoons H_3C-\underset{*}{CH_2} + 2* (\text{or } *)$$

$$H_3C-\underset{*}{CH_2} + \underset{*}{H} \longrightarrow C_2H_6(g) + 2*$$

with the additional features of reversibility in the second step[20] and possible influence upon the effective area of the gaps by the steady-state ratio of coverages by monoadsorbed and diadsorbed alkane.

Of course, the mechanism proposed here for hydrogenations on platinum must be incomplete, since, at least on Pt/Al_2O_3,[20] there are two or more kinds of sites, one of which leads to the formation of olefin-*d* in the presence of deuterium by a process which appears not to be representable in terms of a Horiuti-Polanyi mechanism. Further, as has long been known, there are also processes leading to the formation of slowly reacting species.

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(17) Litvin, E. F.; Kozlova, L. M.; Shapiro, A. B.; Freidlin, L. Kh.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 109–114.

(18) Litvin, E. F.; Kozlova, L. M.; Shapiro, A. B.; Freidlin, L. Kh.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 48–52.

(19) Some of the conclusions in the last section of ref 16 are inconsistent with the model used there and here. They should be replaced with the discussion in the present paper.

(20) Phillipson, J. J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6125–6133.

We think, however, that the proposed mechanism is a good first approximation.

Key experimental aspects of hydrogenation employed in deriving our proposed version of the Horiuti-Polanyi mechanism on platinum are old: the nearly irreversible adsorptions of olefin[11] and of hydrogen.[21] A possible role of gaps in the surface layer in permitting some interconversion of para- and orthohydrogen was proposed long ago.[21] Further, our model has features in common with some other mechanistic proposals. For the hydrogenation of cyclohexene in the vicinity of room temperature, Madon, O'Connell, and Boudart[22] concluded that "the measured rate is that of chemisorption of dihydrogen on a metal surface covered with reactive hydrocarbon intermediate". Although we disagree with their assumption that olefin adsorption is in preequilibrium, for a reaction of zero order in olefin, reversible adsorption will lead to the same kinetic form for the rate (but not for formation of isomerized olefin). Reference 22 also assumes that hydrogen adsorption occurs at gaps in the layer of adsorbed olefin, but it assumes that the adsorption occurs on a carbonaceous layer which almost completely covers the metal. We believe that recent work in this laboratory[23] establishes that at ambient temperatures the hydrogenation reaction occurs directly on the platinum surface. There is also agreement that hydrogen spillover contributes negligibly to the reaction. In particular, we have shown[24] that covering the silica surface of Pt/SiO_2 by $OSi(CH_3)_3$ had a negligible effect upon the rate of hydrogenation of cyclopentene.

In a recent study of the reaction between deuterium and propylene on evaporated rhodium,[25] the rates of desorption of hydrogen and of olefin were both shown to be slow. The authors concluded that "hydrogen adsorption under the retardation of adsorbed propene rate-determines propene hydrogenation over Rh". Despite the nonstandard use of *rate-determining process*,[26] the ideas are close to those expressed in the present paper. The authors[25] consider that the fact that the rate of hydrogenation of ethylene is about twice that of propylene to be "related to adsorption heat of olefin and the number of surface sites occupied by one molecule of adsorbed olefin", whereas we consider the heat of adsorption to be irrelevant once it is strong enough to give zero-order kinetics, and we think it is the gaps in the packing that are determining rather than the number of sites occupied by one molecule of olefin.

Structure Sensitivity. Why should the effect of varying particle size on overall rates of hydrogenation be so small?[12,22] On our model, one must assume that the effective area of the gaps would vary little between various crystal planes and edges. This seems to be a plausible assumption, and it corresponds to that in ref 22 about the effective area of the gaps in a carbonaceous overlayer on these planes and edges. However, structure sensitivity could still be substantial in the selectivities observed in competitive runs, particularly those involving hindered olefins,[12] since selectivity depends upon competition in the adsorption step (like eq 4).

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Registry No. TMPNO, 2564-83-2; TMP, 768-66-1; Pt, 7440-06-4; SiO_2, 7631-86-9; cyclopentene, 142-29-0.

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(21) Eley, D. D. In "Catalysis", Emmett, P. H., Ed.; Reinhold: New York, 1955; Vol. 3, p 63.

(22) Madon, R. J.; O'Connell, J. P.; Boudart, M. *AIChE J.* **1978**, *24*, 904-911.

(23) Hattori, T.; Burwell, R. L., Jr. *J. Phys. Chem.* **1979**, *83*, 241-249.

(24) Kung, H. H.; Brookes, B. I.; Burwell, R. L., Jr. *J. Phys. Chem.* **1974**, *78*, 875-878.

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(26) Boudart, M. "Kinetics of Chemical Processes"; Prentice-Hall: Englewood Cliffs, NJ, 1968.

A Theoretical Study of the Acetaldehyde-Derived Radical

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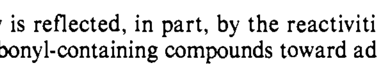
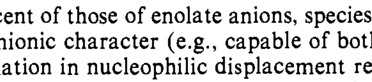
Abstract: Relative stabilities and selected properties for the two lowest lying doublet states of the acetaldehyde-derived radical have been determined with large basis set MCSCF/CI wave functions. The energy gap is seen to be quite sensitive to the choice of basis set and CI orbital space.

The stability of carbon-centered free radicals α to a carbonyl function is generally ascribed to delocalization of the unpaired electron between the carbon atom and the oxygen of the carbonyl function.[1]



This stability is reflected, in part, by the reactivities of α,β-unsaturated carbonyl-containing compounds toward addition by free radicals and hydrogen atom abstraction from the α-carbon of carbonyl-containing compounds. Since the resonance structures of this radical



are reminiscent of those of enolate anions, species which display ambident anionic character (e.g., capable of both C-alkylation and O-alkylation in nucleophilic displacement reactions),[2] ambident character might be expected for α-carbonyl radicals as well. However, there is no experimental evidence for such behavior,

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(1) Walling, C. "Free Radicals in Solution", Wiley: New York, 1957; p 51.

(2) See: Carey, F. A.; Sundberg, R. J. "Advanced Organic Chemistry"; Plenum Press: New York, 1977; pp 15-19.

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