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The Generation of Singlet Oxygen by a Lithium-Tin-Phosphorus Catalyst

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Oxidation catalysts were examined to determine if singlet molecular oxygen ($^1O_2$*) with 23 kcal/mole of excitation energy can be thermally generated and desorbed into a flowing gas stream. Electronically excited oxygen species adsorbed on catalyst surfaces could play an important role in hydrocarbon oxidation processes. Several transition metal oxides and oxidation catalysts were examined in this study. It was found that $^1O_2$* can be thermally generated and desorbed from a lithium-tin-phosphorus catalyst. Rate and temperature effect studies showed that singlet oxygen desorption occurs at $T > 500°C$ and the rate decreases irreversibly to zero after a few hours. The lithium component of the catalyst was found to be important for singlet oxygen generation.

INTRODUCTION

The catalytic oxidation of hydrocarbons has been the subject of many extensive investigations since this reaction is of great importance in modern chemical processes. Many attempts have been made to define the mechanism of catalytic oxidation processes in terms of the nature of the adsorbed oxygen species on catalyst surfaces (*1*). Oxygen ions have been observed on oxide catalysts by ESR and other spectroscopic techniques. Recently it has been proposed that singlet molecular oxygen ($^1\Delta_g$, $^1O_2$*) with 23 kcal/mole of energy above the ground state is formed from O_2^- on transition metal oxides and is the active form of oxygen which interacts with olefins (*2*). Dmuchovsky *et al.* (*3*) have proposed that $^1O_2$* is important in the oxidation of benzene to maleic anhydride over vanadia-molybdena catalysts. Harteck *et al.* (*4*) have observed the formation of electronically excited molecular O_2, N_2, and NO by atom recombination processes on nickel and cobalt. Khan (*5*) has found that $^1O_2$* is formed on hot tungsten filaments and proposed that heterogeneous catalytic oxidation reactions with oxygen could involve $^1O_2$* formation. The primary aim of this work is to determine if singlet oxygen can be generated and desorbed from catalyst surfaces in sufficient quantities to be measured in a flowing gas stream. The thermal generation of $^1O_2$* by catalysts could be an effective source of excited species for hydrocarbon oxidation processes and for synthesis of novel compounds.

Several oxidation catalysts were examined in this study. These include commercial vanadia-molybdena catalysts, supported NiO, MoO_3, Cr_2O_3, CuO, CoO, and Fe_2O_3, and three hydrocarbon oxidative dehydrogenation (OXD) catalysts. The butane OXD catalyst is an unsupported Ni-Sn-P catalyst used to convert *n*-butane to butadiene (*6*, *7*). The oxidative dehydrogenation of alkenes can be carried out using Sn-P and Li-Sn-P catalysts (*8*, *9*).

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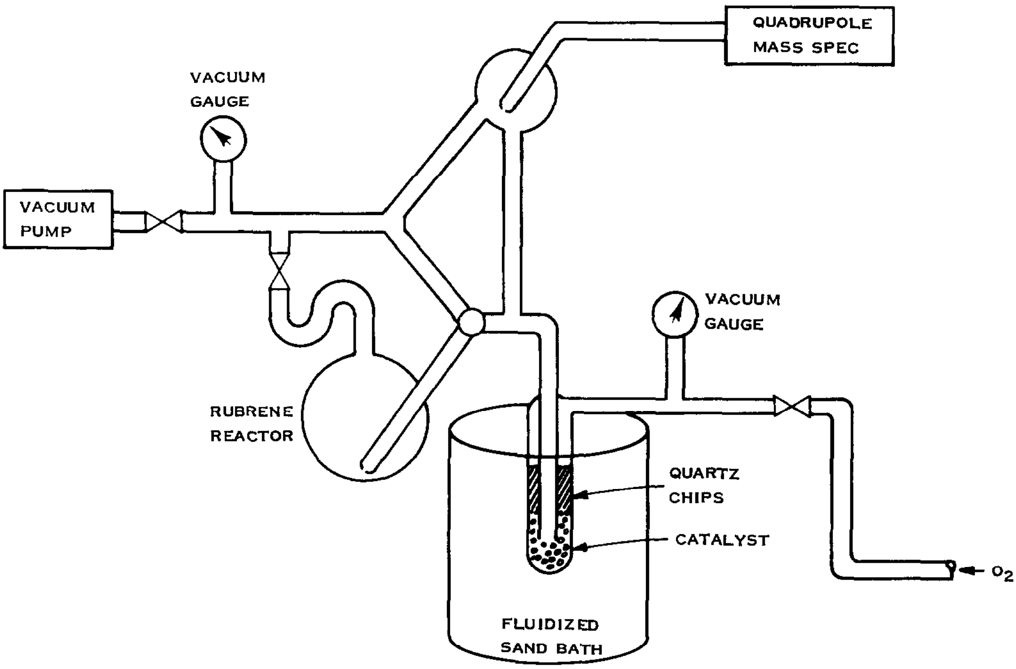

FIG. 1. Flow system used in catalyst–$^1O_2^*$ Studies.

EXPERIMENTAL

The system designed to measure $^1O_2^*$ is shown in Fig. 1. During some experiments, the effluent gas stream from the catalyst was sampled through a small orifice with an Extranuclear Labs quadrupole mass spectrometer (Model 270-9). The mass spectrometer was operated at 10^{-6} Torr of pressure (1 Torr = 133.3 N m^{-2}) in a Varian Model VI-321 high-vacuum system. A Ratheon Microtherm microwave generator operating at 2450 MHz was located upstream from the catalyst bed for external generation of $^1O_2^*$ (*10*). Hydrogen or butene-1 (Phillips Research grade) was introduced into the flow system downstream from the microwave discharge for some studies. Either pure oxygen (Scientific Gas Products, electronic grade) or air was used in all $^1O_2^*$ interaction studies.

Detection of singlet oxygen was accomplished by virtue of its well-known reaction with rubrene (*10*). Rubrene (Aldrich Chemical Co.) is converted to the colorless endoperoxide by $^1O_2^*$ and this change can be measured photometrically. Mallinckrodt bromobenzene was used as the rubrene solvent in experiments of short duration (10 min); hexadecane (Matheson, Coleman and Bell; spectro quality) was used in longer experiments where solvent loss became critical.

Although rubrene reacts primarily with $^1O_2^*$, two other experiments were performed to verify the presence of $^1O_2^*$. Rate constants have been previously reported (*10*) for the quenching of discharge-generated $^1O_2^*$ by 1,4-diazabicyclo [2.2.2] octane (DABCO; Aldrich Chemical Co.) and nickel dibutyldithiocarbamate (BTN; K&K Laboratories). Solutions were prepared of 1.5×10^{-4} M rubrene + 0.5×10^{-4} M BTN in hexadecane. These were then used to react with the $^1O_2^*$ desorbed from catalysts and quenching rate constants [$K(R)$] were determined for each quencher. It has also been reported that CoO is "at least 99% effective" in deactivating $^1O_2^*$

TABLE 1

Catalysts Tested for $^1O_2$* Production[a]

Catalyst	Source[b]	Temperature (°C)	Rubrene (%) converted/hr
Bismuth molybdate	A	400, 500	0, 0
Ni–Sn–P	—	550	0
Li–Sn–P-1	—	650	28[c]
Li–Sn–P-2	—	650	49[c]
Sn–P-3	—	650	1
Sn–P-4	—	650	1
V-1001E, V_2O_5–MoO_3 on alumina	B	400, 650	0, 1
V-1002E, V_2O_5–MoO_3 on alumina	B	400	0
α-Alumina	C	550	0
γ-Alumina	C	600	0
NiO on alumina (15% NiO)	C	300, 600	0,1
Unsupported NiO	D	600	0
MoO_3 on alumina (10–12% MoO_3)	C	600	1
CoO–MoO_3 on alumina (3.5% CoO, 10% MoO_3)	C	600	0
Cr_2O_3 on alumina (7.5% Cr)	C	600	0
Fe_2O_3 on alumina (20% Fe_2O_3)	C	450	0
CuO on alumina (10–12% Cu)	C	350	0
Ag on alumina (~4% Ag)	C	300	0
TiO_2 anatase	E	550	0
ZnO	C	350, 600	0, 0
Manganous–manganic oxides	D	300	1
Cobalto–cobaltic oxides	D	200	1

[a] Oxygen flow rate: 200 cm^3/min.

[b] (A) Girdler Chemical, Inc.; (B) Harshaw Chemical Co.; (C) Strem Chemicals, Inc.; (D) Research Organic–Inorganic Chemical Corp.; (E) Pfaltz & Bauer, Inc.

[c] Estimated uncertainty of ±40%.

(*11*). A grid was constructed from closely spaced pieces of 0.50-mm Co wire from Ventron, cleaned with dilute hydrochloric acid, and oxidized in 10% aqueous NaOH solution for 3 hr. The grid was tested for $^1O_2$* quenching using the microwave-discharge system. It was then placed between the catalyst bed and the rubrene reactor in studies to verify the generation of singlet oxygen by catalysts.

In a typical experiment for studying the thermal generation of $^1O_2$*, 2 g of catalyst (8–16 mesh) is loaded into the quartz catalyst tube. An equal volume of 6- to 8-mesh quartz chips is placed above the catalyst bed to act as a gas preheater. The oxygen flow is started through the catalyst bed. A flow rate of 100–200 cm^3/min (at 1 atm) was found to be the most effective for desorbing singlet oxygen. The pressure downstream from the catalyst bed is maintained at ~4 Torr to minimize collisional deactivation of desorbed $^1O_2$* in the gas stream. The heated sand bath is then raised over the catalyst tube and the catalyst is allowed to equilibrate for 10 min. A Thermo Electric Series 400 thermocouple controller is used for temperature control. After temperature equilibration, the gas flow is diverted into the rubrene reactor containing 10 cm^3 of 1.5×10^{-4} M rubrene in hexadecane for 1–2 hr. The rubrene absorption spectrum is then measured from 400 to 600 nm with a Cary 14 spectrophotometer. The conversion of rubrene to its endoperoxide is determined from the decrease in the absorption maximum at 525 nm.

The Ni–Sn–P catalyst was prepared using the method described by Walker *et al.* (*6*). The samples used in this study contained 49% Ni, 12% Sn, 6.9% P, and 0.5% K. The Li–Sn–P-1 catalyst was prepared by mixing aqueous solutions of stannic chloride and phosphoric acid, forming a precipitate by adding ammonium hydroxide, filtering, washing, drying, forming into ⅛-in. tablets, and calcining at 593°C. The pellets were impregnated with an aqueous lithium nitrate solution and then calcined in air at 677°C. The composition of the finished material was 58.4% Sn, 10% P, and 1.5% Li. The Li–Sn–P-2 sample was prepared by a similar method except the dried precipitate was impregnated with the lithium nitrate solution before tableting into ⅛-in. pellets. The final material composition, weight percentage, was 57.5% Sn, 10% P, and 2% Li. The Sn–P catalysts were prepared by the method described by Pitzer (*8*). Sn–P-3 contained 60.3% Sn and 10.3% P, while the Sn–P-4 catalyst was composed of 60.1% Sn and 10.4% P.

RESULTS

Several typical oxidation catalysts were investigated for generation of singlet oxygen. These heterogeneous catalysts have been reported to be useful in various oxidation reactions (*1–3, 12–14*). The results are reported in Table 1 in terms of rubrene-to-endoperoxide conversion. The temperature of the catalyst bed for each experiment was typical for that particular oxidation process.

TABLE 2

$^1O_2^*$ Production by Li–Sn–P-2 at 650°C[a]

Run No.	Rubrene (%) conversion/hr			
	1st hour	2nd hour	3rd hour	After 15 hr
1	52	25	10	0
2	35	1	—	—
3[b]	22	0	0	—
4[b]	7	1[c]	—	—

[a] O_2 flow rate: 200 cm³/min.

[b] Argon was used instead of O_2.

[c] O_2 was again introduced.

TABLE 3

$^1O_2^*$ Production by Li–Sn–P-2 at Various Temperatures[a]

Temperature (°C)	Rubrene (%) conversion/hr
300	0
500	0
550	0.5[b]
600	5 ± 4[b,c]
650	49 ± 20[c]
700	76

[a] Fresh catalyst sample used at each temperature.

[b] Catalyst preheated for 30 min before run.

[c] Estimated uncertainty.

As shown in Table 1, the only catalysts to desorb significant quantities of $^1O_2^*$ are the Li–Sn–P-1 and Li–Sn–P-2 catalysts. The rate of desorption of singlet oxygen by the Li–Sn–P-2 catalyst is shown in Table 2. These results indicate that the rate of $^1O_2^*$ desorption decreases rapidly with time and approaches zero after a few hours. Significant amounts of $^1O_2^*$ were desorbed from the catalyst even when using an argon stream instead of oxygen (run Nos. 3 and 4). Returning to an oxygen flow after the first hour (run No. 4) did not restore $^1O_2^*$ desorption. Singlet oxygen was also observed from fresh catalysts which had been degassed at room temperature prior to measurements with the $^1O_2^*$ flow system. All these results suggest that: (i) $^1O_2^*$ is formed by O_2 adsorption on catalyst sites which are destroyed during the heating process, and/or (ii) $^1O_2^*$ is produced by the thermal decomposition of some component of the catalyst.

The data in Table 2 indicate poor reproducibility. Glassware cleaning attempts or changing operating conditions (e.g., flow rates) did not eliminate this

TABLE 4

$^1O_2$* Quenching Rate Constants $K(R)$[a]

Quencher	R. F.-Generated $^1O_2$*[a,b]	$^1O_2$* Generated by Li–Sn–P-2[c]
BTN	2.0	7.3
DABCO	0.2	1.0

[a] $K(R)$ proportional to $^1O_2$* quenching rate constant as defined in Ref. (*10*).

[b] Measured with 1.5×10^{-4} M rubrene in bromobenzene at 0°C.

[c] Measured with 1.5×10^{-4} M rubrene in hexadecane at 26°C.

problem. It was observed that hot catalyst fines in direct contact with the rubrene solution cause rubrene oxidation. Consequently, some of these reproducibility problems may be due to catalyst fines carried over into the rubrene solution by the gas stream.

The effect of temperature on $^1O_2$* desorption from the Li–Sn–P-2 catalyst is shown in Table 3. The rate of $^1O_2$* desorption was found to increase with temperature. This is consistent with either a high activation energy for $^1O_2$* production or thermal decomposition of a catalyst component yielding $^1O_2$*.

In order to verify that singlet oxygen is the active species desorbed from the Li–Sn–P catalyst, experiments were conducted using known $^1O_2$* quenchers other than rubrene. Relative quenching rate constants for two known $^1O_2$* quenchers, BTN and DABCO, were determined and the results are given in Table 4.

Although the $K(R)$ values determined for BTN and DABCO for the microwave-discharge study are different from those measured in the catalyst experiments, the trends and the ratio of $K(R)$ values for BTN/DABCO are similar. Solvent effects (*15*) can easily account for the difference in magnitude of $K(R)$.

It has been reported that CoO wire functions as an effective quencher of singlet oxygen (*11*). This is verified by the data in Table 5 for $^1O_2$* generated by a microwave discharge. Quenching is also observed for the active species desorbed from the heated Li–Sn–P-2 catalyst. Complete quenching is not observed in the latter case because of the high oxygen flow rate. It should be noted that, during the course of these BTN, DABCO, and CoO wire-quenching experiments (~2-week lapse time), good reproducibility was obtained with the heated catalyst experiment. Seven runs over this period with a 200-cm³/min oxygen flow rate and the Li–Sn–P-2 catalyst at 650°C gave a rubrene conversion of 16 ± 4%. Modifications made to the rubrene reactor before these experiments are probably responsible for the reduced rubrene conversion.

TABLE 5

$^1O_2$* Quenching by Wire Grid

	R. F.-Generated $^1O_2$*	Li–Sn–P-2-Generated $^1O_2$*[a]
Co grid unoxidized[b]	62	—
Without grid[b]	60	17[c]
Oxidized grid[b]	5	8[c]
$^1O_2$* Deactivated (%)	92	53
O_2 flow rate (ml/min)	20	200
Run time (min)	1	120

[a] Catalyst preheated for 30 min.

[b] Indicated as percentage of rubrene converted.

[c] Catalyst temperature is 650°C.

TABLE 6

$^1O_2$* Production at 650°C

	Rubrene (%) conversion/hr
Li–Sn–P-1	28, 27[a]
Sn–P-3	1
Sn–P-4	1
Stannic oxide	1
Stannic phosphate	0
Stannous pyrophosphate	0
Lithium orthophosphate (primary)	0
Lithium orthophosphate (tertiary)	0
Ammonium sulfate	1
Ammonium phosphate	2

[a] Two separate runs.

In an attempt to determine the mechanism of $^1O_2^*$ production by the Li–Sn–P catalyst, several similar catalysts and catalyst components were examined. The results are given in Table 6. It is significant that, although $^1O_2^*$ desorption was observed from the Li–Sn–P catalyst, little singlet oxygen was measured from the Sn–P-3 and Sn–P-4 catalysts, SnO_2, or any of the single catalyst components listed in Table 6. Clearly, these results indicate that the lithium component in the calcined catalyst is important for singlet oxygen production.

The effect of catalyst reduction by hydrogen and butene on singlet oxygen production was also investigated. Experiments were conducted with the Li–Sn–P-1 catalyst at 650°C and a flow rate of 200 cm^3/min of oxygen with 1% hydrogen. Introduction of hydrogen in the flow system was found to reduce the rubrene conversion from 27 to 1%. Essentially the same results were obtained with butene-1 in place of hydrogen. These results are not due to the gas-phase reaction of $^1O_2^*$ with H_2 or butene-1 since no reaction products could be detected with the quadrupole mass spectrometer, even for butene-1 with discharge-generated $^1O_2^*$. Apparently, hydrogen and butene-1 reduce the catalyst surface to destroy the active sites for $^1O_2^*$.

SUMMARY AND CONCLUSIONS

In this study we have shown that singlet oxygen with 23 kcal/mole of excitation energy is generated and desorbed from the Li–Sn–P catalyst. No other heterogeneous oxidation catalysts were found to desorb significant quantities of $^1O_2^*$. Dmuchovsky *et al.* (*3*) have proposed that $^1O_2^*$ is important in the oxidation of benzene and maleic anhydride over vanadia–molybdena catalysts, and Krylov (*2*) has suggested that singlet oxygen plays an important role in the selectivity of transition metal oxide catalyst. However, we are unable to verify that similar catalysts desorb singlet oxygen. It may be possible that $^1O_2^*$ is indeed generated on some of these oxidative catalysts but deactivates before desorption. Detection of singlet oxygen adsorbed on catalyst surfaces would require emission techniques and single-photon counting which is beyond the scope of this study.

The rate of $^1O_2^*$ desorption from the Li–Sn–P catalyst was found to increase rapidly with temperature but decrease with heating time. Studies of the individual components of this catalyst indicate that Li in the catalyst is necessary for $^1O_2^*$ generation. However, the mechanism of singlet oxygen production is still not clear. Whether or not a superoxide is formed by lithium doping which leads to $^1O_2^*$ formation is yet to be determined. Superoxides have been shown to liberate singlet oxygen under certain conditions (*16*). Further studies are necessary to determine the role played by singlet oxygen in oxidation processes.

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