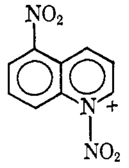
pattern, partial rate factors, and substrate selectivities for these salts are summarized in Table I.

As anticipated from our results in the pyridine series, the *peri* interaction in N-nitroquinoline sufficiently weakens the N–N bond and allows transfer nitration to occur readily. The enhanced reactivity of the N-nitroquinoline **5** (Table I) illustrates further the importance



5

of base strength in determining reactivities of N-nitro compounds.[14] Particularly noteworthy is the small but significant decrease in positional selectivity observed for **5** despite its lower substrate selectivity. The factors responsible for this behavior along with related mechanistic studies of these reactions are currently under investigation.

(14) It is tempting to ascribe the increased reactivity of **5**, in comparison with the N-nitropyridinium salts, solely to the reduced basicity of the quinoline. However, the importance of solvent in determining reactivity remains to be studied.

(15) National Defense Education Act Fellow, 1965–1968.

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The Free-Radical Nature of Chlorotris(triphenylphosphine)rhodium-Catalyzed Autoxidations of Cyclohexene and Ethylbenzene

Sir:

Chlorotris(triphenylphosphine)rhodium [$(Ph_3P)_3RhCl$] is a well-known, potent homogeneous hydrogenation catalyst.[1] Its catalytic properties in oxidation reactions with molecular oxygen were recently reported[2–5] and postulated[2–4] to involve unique oxygen activation by coordinatively unsaturated d^8 complexes. We now wish to present evidence that autoxidations of cyclohexene and ethylbenzene catalyzed by $(Ph_3P)_3RhCl$ are free-radical chain oxidations.[6]

We compared the products and the over-all rates of oxidation[7] in the presence of $(Ph_3P)_3RhCl$ with those using rhodium acetylacetonate [$Rh(AcAc)_3$], rhodium 2-ethylhexanoate [$Rh(2\text{-}EH)_3$], and cobalt 2-ethylhexanoate [$Co(2\text{-}EH)_2$]. The results of cyclohexene autoxidations are in Table I.

Table I. Products of Metal-Catalyzed Autoxidations of Cyclohexene at 60°[a]

			Yield, %			
Catalyst[b]	Time, hr	Convn, %	2-Cyclohexen-1-one[c]	2-Cyclohexen-1-ol[c,d]	Hydroperoxide[e]	Other[f]
$(Ph_3P)_3RhCl$	10	63	35	28	27	14
$Rh(AcAc)_3$	10	78	51	20	18	11
$Rh(2\text{-}EH)_3$	10	62	57	20	15	8
$Co(2\text{-}EH)_2$	10	79	48	20	21	11
$(Ph_3P)_3RhCl$[g]	10	0				
None	10	1				

[a] Oxidation reactions were 4.8 *M* in cyclohexene (Phillips 99%, silica gel treated) and 2.9 × 10^{-3} *M* in catalyst [$(Ph_3P)_3RhCl$ was 1.4 × 10^{-3} *M*] in benzene. [b] 2-Ethylhexanoates were prepared by the method of J. F. Harrod and A. J. Chalk (*J. Am. Chem. Soc.*, **86**, 1776 (1964)). Other compounds were commercial chemicals. [c] Determined by glpc after reduction with Ph_3P. Identities were confirmed by comparison of ir and mass spectra of trapped samples with reference spectra. [d] Carbinol product is total carbinol[c] minus hydroperoxide. [e] Determined iodometrically. [f] Unidentified products. [g] In the presence of 2 mol % of hydroquinone.

All three rhodium compounds catalyze autoxidation of cyclohexene and yield similar product mixtures. Furthermore, cobalt 2-ethylhexanoate catalyzed autoxidation shows an almost identical product distribution. 2-Cyclohexen-1-yl hydroperoxide, the major product from thermal autoxidation of cyclohexene,[8] was found in all metal-catalyzed oxidations. The α,β-unsaturated alcohol and ketone are secondary products which arise from the initially formed hydroperoxide. The chain nature of the reaction is demonstrated by complete inhibition of the oxidation by 2% of hydroquinone.

In the case of ethylbenzene autoxidations (Table II), the similarity in the product distribution is even more striking. Only traces of hydroperoxide were detected in these oxidations. In addition to the indicated products, small amounts of benzoic acid were formed by complete side-chain oxidation. Again, the reaction was completely inhibited by a free-radical inhibitor. With both substrates the uncatalyzed reactions were much slower than the metal-catalyzed oxidations.

Table II. Products of Metal-Catalyzed Autoxidations of Ethylbenzene at 130°[a]

			Yield, %		
Catalyst[b]	Time, hr	Convn, %	Acetophenone[c]	1-Phenylethanol[c,d]	Hydroperoxide[e]
$(Ph_3P)_3RhCl$	2	8	66	33	3
	10	34	80	19	2
$Rh(AcAc)_3$	2	10	60	40	2
	10	29	80	20	1
$Rh(2\text{-}EH)_3$	2	13	67	33	2
	10	36	82	18	1
$Co(2\text{-}EH)_2$	2	8	76	24	2
	10	63	92	8	0
$(Ph_3P)_3RhCl$[f]	10	0			
None	10	8	20	2	76

[a] Neat ethylbenzene containing 4.8 × 10^{-3} *M* catalyst [$Co(2\text{-}EH)_2$ was 8.2 × 10^{-3} *M*]. [b–e] See corresponding footnotes in Table I. [f] In the presence of 1 mol % of 6-*t*-butyl-*o*-cresol.

In separate experiments we showed that $(Ph_3P)_3RhCl$–*t*-butyl hydroperoxide system initiates rapid polymeriza-

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(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(2) J. P. Collman, M. Kubota, and J. W. Hosking, *J. Am. Chem. Soc.*, **89**, 4809 (1967).

(3) J. Blum, H. Rosenman, and E. D. Bergmann, *Tetrahedron Letters*, 3665 (1967).

(4) J. Blum and H. Rosenman, *Israel J. Chem.*, **5**, 69 (1967).

(5) A. J. Birch and G. S. R. Subba Rao, *Tetrahedron Letters*, 2917 (1968).

(6) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968), recently suggested that some oxidations catalyzed by d^8 complexes might be free-radical reactions.

(7) The oxidations were carried out in cylindrical glass vessels provided with an efficient stirrer, external heater, air-inlet tube, and reflux condenser.

(8) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Am. Chem. Soc.*, **87**, 4824 (1965).

tion of styrene. Control reactions which contained $(Ph_3P)_3RhCl$ and styrene, and *t*-butyl hydroperoxide and styrene, were much slower.

Rhodium(I) and rhodium(III) compounds appear to be equally active and give similar product mixtures. It is clear that rhodium must change its oxidation state in the course of these reactions. The nature and spatial arrangement of ligands around rhodium do not have a profound effect on the course of these oxidations. The geometries of rhodium(I) and rhodium(III) must be different[9] and must change during the oxidation as a result of changes in the oxidation state of rhodium.

These arguments, together with the inhibition, polymerization, and product studies, are compatible only with a free-radical chain mechanism. We propose that rhodium, by analogy with cobalt, catalyzes chain initiation by a Haber–Weiss type mechanism.[10] A similar mechanism can be written involving Rh(I) and Rh(II) species.

$$\mathrm{ROOH + Rh(III) \longrightarrow ROO\cdot + H^+ + Rh(II)}$$

$$\mathrm{ROOH + Rh(II) \longrightarrow RO\cdot + OH^- + Rh(III)}^{11}$$

Rhodium(II) is not a common oxidation state of rhodium, but it may be an intermediate in redox reactions.[12]

An alternative mechanism involving a two-electron transfer is possible. This mechanism requires a termolecular reaction and seems less likely to occur.

$$\mathrm{2ROOH + Rh(III) \longrightarrow 2ROO\cdot + 2H^+ + Rh(I)}$$

$$\mathrm{2ROOH + Rh(I) \longrightarrow 2RO\cdot + 2OH^- + Rh(III)}$$

At this point it is difficult to say anything about the detailed mechanism of the electron transfer; however, in the case of cobalt,[13,14] it was shown that electron transfer involves a prior complex formation between the hydroperoxide and the catalyst.

Acknowledgments. We wish to thank Professor S. Winstein for helpful discussions and Mr. L. R. Bruner for technical assistance.

(9) By analogy with other rhodium(I) complexes, $(Ph_3P)_3RhCl$ is probably square planar, whereas rhodium(III) acetylacetonate is most likely octahedral.

(10) F. Haber and J. Weiss, *Naturwissenschaften*, **20**, 948 (1932).

(11) Rh(II) and Rh(III) stand for covalently bound rhodium as is the case in nonpolar organic media.

(12) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1966, p 1009.

(13) A. J. Chalk and J. F. Smith, *Trans. Faraday Soc.*, 1214 (1957).

(14) E. Ochiai, *Tetrahedron*, **20**, 1819 (1964).

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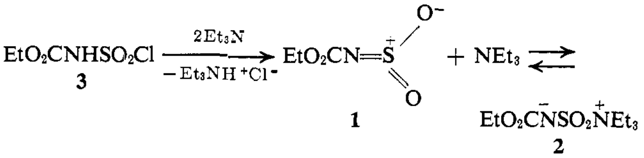
The Reactions of an N-Sulfonylamine Inner Salt

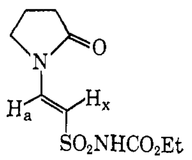
Sir:

We have previously reported a general method for the synthesis of a new heterocumulene system, the N-sulfonylamine.[1] To extend our studies on the cycloadditive reactivity of electrophilic N-sulfonylamines with olefins we have generated the rigid[2] N-sulfonylamine, ethyl N-sulfonylcarbamate (**1**), *via* fragmentation of the inner salt **2**. We now wish to report our observations on the synthesis and reactions of **2**.

Carbethoxysulfamoyl chloride[3] (**3**) reacts rapidly with 2 equiv of triethylamine in benzene solution at 30° to provide an 81% yield of crystalline ethyl (carboxysulfamoyl)triethylammonium hydroxide inner salt (**2**), mp 66–69°.[4,5] Consistent with the proposed structure, **2** displayed nmr (benzene, 60 Mc) resonances at τ 5.71 (quartet, 2 H), 8.72 (triplet, 3 H), 6.71 (quartet, 6 H), and 8.85 (triplet, 9 H), and a low-energy carbonyl stretching frequency at 1685 cm^{-1} in the infrared. A benzene solution of **2** exothermally reacts with aniline to afford a 92% yield of N-carbethoxy-N′-phenylsulfamide (**4a**),[6,7] while 2-propanol more slowly yields isopropyl carboethoxysulfamate (**4b**),[8] and N,N,dimethylaniline likewise provides N,N-dimethyl-N′-carbethoxysulfanilamide.[6,9]



3 **1** **2**



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$\mathrm{EtO_2CNHSO_2R}$

4a, $\mathrm{R = NHC_6H_6}$
b, $\mathrm{R = OCH(CH_3)_2}$

The inner salt **2** undergoes electrophilic addition to N-vinylpyrolidinone in benzene solution at 50° to yield 50% of N-(2-carbethoxyamidosulfonylvinyl)pyrrolidone (**5**), mp 150°.[10]

The nmr spectrum ($CDCl_3$, 60 Mc) of **5** indicated a doublet for H_x centered at τ 4.02 coupled (J = 14 Hz) with the signal of H_a centered at τ 1.89. We were unable to detect the intermediacy of the substituted 1,2-thiazetidene 1,1-dioxide cycloadduct whose base-catalyzed ring opening to **5** would be expected under these conditions.[1]

Treatment of **2** in acetonitrile solution at 60° with tetramethylallene provided a 60% yield of two isomeric cycloadducts, **6** and **7**, in a ratio of 1:5. 2,3-Dihydro-2,2-dimethyl-3-isopropylidene-6-ethoxy-1,4,5-oxathiazine 4,4-dioxide (**7**), mp 81–82°, exhibited nmr ($CDCl_3$,

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(1) G. M. Atkins and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

(2) We have found that the reaction of N-sulfonylbenzamide ($C_6H_5CON{=}SO_2$) with weakly nucleophilic olefins competes with its rearrangement to phenyl isocyanate. See ref 1.

(3) Prepared by the interaction of absolute ethanol with chlorosulfonyl isocyanate: A. Dorlars in Houben-Weyl's "Methoden der Organischen Chemie," Vol. 8, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, Germany, 1952, p 700.

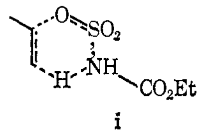
(4) An inner salt derived from N-sulfonylsulfamide ($H_2NSO_2N{=}SO_2$) has been reported recently: R. Appel and R. Helwerth, *Angew. Chem.*, **79**, 937 (1967).

(5) Satisfactory elemental and mass spectral analyses were obtained for all new compounds reported herein.

(6) Identified by mixture melting point and infrared spectral comparison with an authentic sample.

(7) R. Graf, German Patent 940,292 (1956); *Chem. Abstr.*, **52**, 14667*c* (1959).

(8) We have noted that this sulfamate ester underwent a facile fragmentation at temperatures as low as 60°, possibly *via* the cyclic transition state **i**, to provide propene, sulfur trioxide, and ethyl carbamate.



i

(9) Belgian Patent 622,214 (1963); *Chem. Abstr.*, **59**, 12710*d* (1963).

(10) An analogous reaction occurred with ethyl vinyl ether.