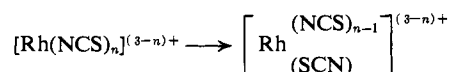


soft. We succeeded in preparing the two linkage isomers of thiocyanatopentaamminerhodium(III) and -iridium(III) by refluxing the aquopentaammines with an excess of NaSCN in aqueous solution. The characterization of the compounds and their assignments are given below. By far the largest part (~60–70%) of the yielded product represents the nitrogen-bonded isomer (isothiocyanate). The other components are formed only in small yields (some 10%). Prolonged boiling of the reaction mixture decreases the yield of the sulfur-bonded (thiocyanate) complexes. Already from this relation we may conclude that the nitrogen-bonded isomers are the more stable components. Kinetic experiments performed at 40° indicate negligible conversion of the two isomers into each other after 48 hr., but an appreciable rearrangement of the sulfur-bonded Rh isomer into the nitrogen-bonded component can be observed after 3 hr. at 78°. However, the reaction cannot be followed completely since decomposition products are formed. The first-order rate constant for this reaction calculated for the first 50 hr. is $k = 2.7 \times 10^{-6} \text{ sec.}^{-1}$. The nitrogen-bonded Rh complex, on the other hand, does not show any tendency for isomerization at 78° but yields distinct decomposition products even after 24 hr. Addition of alcohol does not accelerate the attainment of the equilibrium but facilitates the formation of decomposition products.

These experiments apparently confirm the class (a) behavior of the radicals $[\text{Rh}(\text{NH}_3)_5]^{3+}$ and $[\text{Ir}(\text{NH}_3)_5]^{3+}$, but do not enable the classification of the free ions. The softness of the bare ions is suggested by the observation that all the thiocyanate ligands in $[\text{Rh}(\text{SCN})_6]^{3-}$ are bonded through the sulfur.^{7,8} If in the reaction



series the first SCN^- ($n = 0$) is bonded through the sulfur atom, all the other SCN^- ($n = 1$ to 5) also enter through sulfur, since each additional ligand makes the central atom site softer. In this case, class (b) character is obvious for free Rh^{3+} . On the other hand, class (a) character would be deduced if the first SCN^- ($n = 0$) were bonded through nitrogen. In this case we distinguish between two possibilities. If N-coordinated NCS^- made the Rh site harder, then the linkage properties of $[\text{Rh}(\text{SCN})_6]^{3-}$ could not be explained. The other more improbable case is that the Rh site gets softer upon coordination through the nitrogen atom. Then at a certain n , a rearrangement process



has to take place. This reaction or some other one may think of can only go through a bimolecular path, since the species $[\text{Rh}(\text{NCS})_{n-1}]$ appearing in a monomolecular process was assumed to be hard in the reaction series. Rearrangement reactions of this kind, however, are observed to have monomolecular paths.^{9,10} The above arguments still hold in solution when the other ligand sites are occupied by hard solvent molecules (e.g., H_2O). Further evidence for the softness of Rh^{3+} and Ir^{3+} is the high insolubility of their iodides compared with their chlorides and bromides. Solubil-

ity arguments can be employed when solvation effects are neglected. As for rhodium, we would rather suggest softness for iridium, following the usual trend within a group of the periodic table.¹ For lower oxidation states an even softer behavior is expected.

The characterization and assignment of the acidopentaammines by spectroscopic investigations are given in Tables I and II.

Table I. Visible and Ultraviolet Spectra^a

$\lambda, \text{m}\mu$	ϵ	$\lambda, \text{m}\mu$	ϵ
N-Bonded Rh Isomer		S-Bonded Rh Isomer	
320	460	375	85
(240)	2200	323	220
(215)	5100	(280)	450
		233	19,200
N-Bonded Ir Isomer		S-Bonded Ir Isomer	
(330)	64	(355)	35
(260)	550	(310)	100
(230)	2000	(275)	180

^a Band maxima in $\text{m}\mu$ and molar extinction coefficients ϵ (band shoulders in brackets). The assignments in Table I are made according to the spectrochemical series.¹¹

Table II. Infrared Spectra^a

N-Bonded Rh Isomer		S-Bonded Rh Isomer	
C–N stretch, 2145 (s, b)		2115 (s, sp)	
C–S stretch, 815 (s)		730 (w, b)	
N-Bonded Ir Isomer		S-Bonded Ir Isomer	
C–N stretch, 2140 (s, b)		2110 (s, sp)	
C–S stretch, 825 (s)		700 (m)	

^a Fundamental frequencies in cm.^{-1} of the SCN group of samples in KBr disks. Abbreviations: s, strong; m, medium; w, weak; b, broad; sp, sharp.

According to Turco and Pecile⁵ and Tramer,¹² only the position of the C–S stretching frequency can serve as a criterion for the assignment of the two linkage isomers. The bands found are actually in the region given by these authors being characteristic of the two isomers.

(11) See C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

(12) A. Tramer, *J. chim. phys.*, **59**, 232 (1962).

H.-H. Schmidtke

Cyanamid European Research Institute
Cologny, Geneva, Switzerland

Received March 27, 1965

Anionic Oxidation of Simple Alkyl Aromatics

Sir:

Although the base-catalyzed oxidation of hydrocarbon and related materials has received considerable attention by Russell,¹ the compounds studied were necessarily of a group possessing a readily ionized C–H bond. This restriction was imposed by the presence of dimethyl sulfoxide which itself is reactive with molecular oxygen unless it is diluted with considerable proportions

(7) Z. V. Zvonkova, *Zh. Fiz. Khim.*, **27**, 100 (1953).

(8) H.-H. Schmidtke, *Z. physik. Chem.* (Frankfurt), **40**, 96 (1964).

(9) F. Basolo and G. S. Hamaker, *Inorg. Chem.*, **1**, 1 (1962).

(10) J. L. Burmeister and F. Basolo, *ibid.*, **3**, 1587 (1964).

(1) G. A. Russell, *J. Am. Chem. Soc.*, **76**, 1595 (1954); G. A. Russell, E. G. Jansen, H. D. Becker, and F. Smentkowski, *ibid.*, **84**, 2652 (1962); G. A. Russell, A. J. Moye, and K. Nagpal, *ibid.*, **84**, 4154 (1962).

of alcohol. It has been recently reported² that diphenyl sulfoxide at 100° is a base- and oxygen-stable solvent capable of promoting the base-catalyzed oxidation of alkyl aromatics to aromatic acids. We now wish to report a system that is much more effective than diphenyl sulfoxide in promoting base-catalyzed oxidation of alkyl aromatics to carboxylic acids. This system consists of a base such as potassium *t*-butoxide or even potassium hydroxide in hexamethylphosphoramide. The system is fluid and operative at room temperature and provides a new technique for the selective oxidation of alkyl aromatics with varying side chains to the corresponding aromatic carboxylic acid.

This work was carried out by contacting the aromatic hydrocarbon (0.24 *M* for toluene, ethylbenzene, and *p*-cymene, and 0.12 *M* for the xylenes and tetralin) at room temperature with molecular oxygen in the presence of a 0.7 *M* solution of potassium *t*-butoxide in hexamethylphosphoramide (HMPA). The experimental apparatus was essentially identical with that described by Bartok, *et al.*³ Rates of oxygen absorption were monitored for each reaction and, after isolation, individual products were identified by infrared, ultraviolet, and elemental analyses.

In each case, the major product was the corresponding aryl mono- and dicarboxylic acid (see Table I). For the

Table I

Reactant	Rel. rate ^a	Product acid	Yield, mole %
Toluene	1.0	Benzoic	25-30
<i>o</i> -Xylene	3.1	Phthalic	35-40
<i>m</i> -Xylene	0.5	Isophthalic	50
<i>p</i> -Xylene	0.1	Terephthalic	15
Ethylbenzene		Benzoic	11
<i>p</i> -Cymene	1.0	<i>p</i> -Isopropylbenzoic	10
Tetralin	1.0	Phthalic	46

^a Based on the initial rate of O₂ absorption.

three xylenes only very minor amounts of the corresponding toluic acids were found. In all cases the formation of dimeric products, such as bibenzyl and stilbene from toluene, were essentially nonexistent. As examples of the absolute rate of reaction, one-half of the maximum conversion of *o*-xylene is obtained in about 1 hr. at room temperature, while for an equivalent conversion toluene takes *ca.* 3 hr. Reaction rates do decrease with time; this is due to consumption of the base by the acid product and the buildup of both alcohol and water in the solvent.

The over-all course of reaction is undoubtedly similar to that described by Russell.⁴ Basically this involves ionization of the benzylic C-H bond, transfer of an electron to oxygen to form a benzyl radical, and finally autoxidation of the radical. Ionization of the initial C-H bond appears to be the rate-determining step as the

(2) T. J. Wallace, A. Schriesheim, and N. Jacobson, Preprint, Petroleum Division of the American Chemical Society, 9, No. 4, D-145 (1964).

(3) W. Bartok, D. D. Rosenfeld, and A. Schriesheim, *J. Org. Chem.*, 28, 410 (1963).

(4) G. A. Russell, Preprints, 17th National Organic Symposium, Bloomington, Ind., June 25-29, 1961.

relative rates of initial oxygen absorption, 3.1 for *o*-xylene, 1.0 for toluene, 0.5 for *m*-xylene, and 0.1 for *p*-xylene, are in good agreement with the relative rates of reactivity for each of these alkyl aromatics as determined by isotope exchange with dimethyl sulfoxide.⁵ Also, in the case of *p*-cymene, the most acidic hydrogens according to relative ionization rate measurements are oxidized preferentially and only *p*-isopropylbenzoic acid is formed. The formation of only minor amounts of the monobasic acids from the xylene isomers is indicative of a stepwise reaction where the oxidation of the second methyl group proceeds more rapidly than the first. This arises because of the rate-accelerating tendency of the first carboxyl group and, in the case of *m*- and *p*-xylene, the elimination of the rather pronounced rate-retarding tendency of the original methyl groups.⁵

The ability to oxidize materials rapidly in basic media that are as weakly acidic as toluene and the xylenes is clearly the result of the use of a solvent such as HMPA. There are apparently several reasons for this. First, the hydrogens on HMPA appear to be completely unreactive toward base. We have attempted to carry out base-catalyzed proton exchange reactions between toluene, labeled with tritium in the methyl group, and various dipolar solvents. Of those listed in Table II, HMPA was the only one that under-

Table II

Solvent	Time ^a
Hexamethylphosphoramide	>14,400
Tetramethylene sulfoxide	420
N-Methyl-2-pyrrolidone	48
Dimethyl sulfone	12
Dimethyl sulfoxide	6

^a For 10% exchange at 55°, min.

went no detectable exchange. Also, HMPA in the presence of base is essentially unreactive toward oxygen. Second, HMPA promotes the ionization of hydrocarbons at a rate that may be even somewhat greater than would be expected for its dielectric constant ($\epsilon = 30$ at 25°). This may be due to the special ability of HMPA to solvate the carbanion or the alcohol produced during hydrocarbon ionization. Finally, HMPA has a low melting point, 4°, and a high boiling point, 232°, which permits its use over a wide range of conditions.

The present work regarding oxidation reactions has been extended to a number of other hydrocarbons, and a more extensive report will be prepared in the near future.

(5) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *J. Am. Chem. Soc.*, 85, 3002 (1963).

(6) Reaction rates vs. solvent polarity will be the subject of subsequent papers from this laboratory.

J. E. Hofmann, A. Schriesheim, D. D. Rosenfeld

Process Research Division
Esso Research and Engineering Co.
Linden, New Jersey

Received March 8, 1965