apart from solvation of $NiCl_3^-$, *i.e.*, n is unity. This fitting was done by digital computer which simultaneously generated k_3 values and the spectra of the component species. The latter are shown in Figure 1. Band maxima for $NiCl_3^-$ are at 13,100 and 17,700 cm^{-1}. The quantity log k_3 was a linear function of $1/T$ over the range 500–750°.

From the temperature dependence of k_1, k_2, and k_3 it was found that $\Delta H_1° \cong 25.8$ kcal, $\Delta S_1° \cong 23.5$ cal/deg, $\Delta H_2° = 13.1$ kcal, $\Delta S_2° \cong 14.6$ cal/deg, $\Delta H_3° = (13.3 \pm 0.2)$ kcal, and $\Delta S_3° = (9.8 \pm 0.1)$ cal/deg. Since eq 1, 2, and 3 are interdependent, $\Delta H_3° - \Delta H_2° + \Delta H_1°$ and $\Delta S_3° - \Delta S_2° + \Delta S_1°$ should equal zero, which they do to within experimental uncertainty.

The spectrum of $NiCl_3^-$ differs markedly from the spectra for approximately octahedral[1-3] and approximately tetrahedral[3,4] chloronickel(II) entities in crystals, molten salts, and other solutions. In this respect the absence of a spin-allowed band between 5000 and 13,000 cm^{-1} is noteworthy. This result rules against the monosolvated species $NiCl_3AlCl_4^{2-}$, which, in analogy to $NiCl_3ZnCl_4^{3-}$, would be expected to consist of ($NiCl_4$) and ($AlCl_4$) tetrahedra that share a corner.[4] Øye and Gruen[5] have given preliminary evidence for precisely this entity in liquid $KAlCl_4$.

The unusual spectrum of $NiCl_3^-$ is satisfactorily rationalized in terms of D_{3h} point group geometry. Computer calculations of the energy levels for this geometry utilized the tensor operator equations described by Wybourne[6] with B_0^2 and B_0^4 as potential parameters. Values of the two electronic repulsion parameters and the spin-orbit coupling constant were the same as those used by DeKock and Gruen[7] for gaseous $NiCl_2$. (The latter three parameters have about the same values for all chloronickel(II) entities.) Best fits between calculated and observed transition energies were achieved with $B_0^2/B_0^4 = -8/3$ and 5/3. In the electrostatic point-charge model the former corresponds to a weak axial perturbation and the latter to a strong axial perturbation, *i.e.*, $NiCl_3(AlCl_4)_2^{3-}$. The latter entity cannot be reconciled with the large, positive value as $\Delta S_3°$ unless the reaction is accompanied by a large structural change in the solvent. But the available evidence indicates that liquid alkali metal tetrachloroaluminates containing an excess of alkali metal chloride do not have elaborate or rigid interionic structures.[5,8-12] For this reason we discard the five-coordinate entity $NiCl_3(AlCl_4)_2^{3-}$ as very improbable and conclude that $NiCl_3^-$ is not complexed to solvent ions. It is, of course, weakly perturbed by the coulomb field due to solvent ions above and below the molecular plane in a way that is analogous to the perturbation of nitrate ions by surrounding ions in a molten alkali metal nitrate.

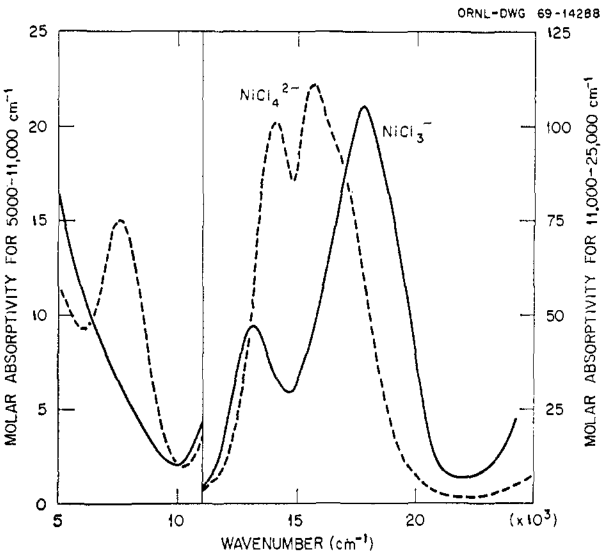

Figure 1. Spectra of $NiCl_4^{2-}$ and $NiCl_3^-$ in molten $CsAlCl_4$ containing small amounts of added CsCl at 600°. Calculated from spectra of mixtures using exprimental k_3 value.

Final values of B_0^2 and B_0^4 for $NiCl_3^-$ were 13,300 and -3900 cm^{-1}, respectively. These compare[7] with $-12{,}600$ and -4200 cm^{-1}, respectively, for gaseous $NiCl_2$ and, hence, have a reasonable magnitude.

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Photodimerization of Norbornadiene Using Chromium Hexacarbonyl

Sir:

During the course of our investigations into the mechanistic details of metal carbonyl assisted photodimerization of norbornadiene,[1] we have extended the number of useful metal carbonyls and identified one of the intermediates in the reaction.

Norbornadiene was first dimerized photochemically by Pettit[2] using $Fe(CO)_5$, and the reaction was further characterized by Lemal.[3] Other workers have shown that norbornadiene can be dimerized thermally using $Ni(CO)_4$,[4] $((C_6H_5)_3P)_2Co_2(CO)_6$,[5] $Fe(NO)_2(CO)_2$,[6] $Co(CO)_3NO$,[6] and $Fe_2(CO)_9$.[7] Schrauzer has added other olefins to norbornadiene thermally and suggested

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(1) Bicyclo[2.2.1]hepta-2,5-diene.

(2) R. Pettit, *J. Amer. Chem. Soc.*, **81**, 1266 (1959).

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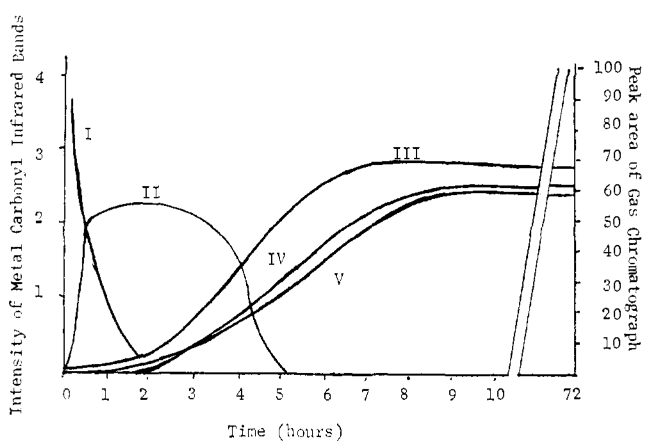
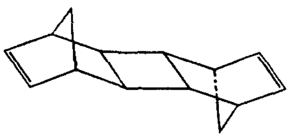


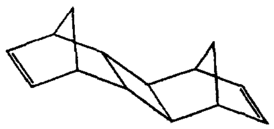
Figure 1. Plot of peak areas from vapor phase chromatography of products *vs.* time and plot of infrared band intensity of the metal carbonyls *vs.* time: (I) chromium hexacarbonyl, (II) norbornadiene tetracarbonyl, (III) *exo-trans-exo* dimer, (IV) *endo-trans-endo* dimer, (V) *exo-trans-endo* dimer.

mechanisms for the reaction. All of these aspects are covered in his review article.[8]

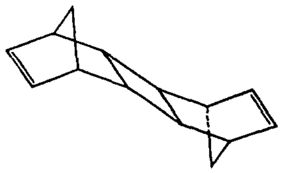
In the cyclobutane dimers of norbornadiene, there are six possible stereochemically isomeric compounds. To date, however, only three have been prepared.



I
(*exo-trans-exo*)



II
(*endo-trans-exo*)



III
(*endo-trans-endo*)

The number and type of dimers produced are apparently dependent upon the type of transition metal complex and upon the conditions of the reactions, either thermal or photochemical. Other compounds which have been dimerized thermally with transition metals are benzonorbornadiene,[9] allene,[10] and butadiene.[11]

Jolly[6] has suggested that a dinorbornadiene-iron-dinitrosyl complex is present and perhaps is the reaction intermediate in the thermal dimerization of norbornadiene using $Fe(NO)_2(CO)_2$. Unfortunately, this proposed intermediate has not been isolated. This suggests that norbornadienemetal carbonyl intermediates might be present in other cases, and perhaps conclusive evidence could be obtained to prove their existence. Indeed, this is the case, as we have shown that norbornadienechromiumtetracarbonyl is one of the intermediates in the $Cr(CO)_6$-assisted dimerization of norbornadiene. This conclusion is based on the following data: (a) norbornadienechromium tetracarbonyl has been isolated from the reaction; (b) irradiation of norbornadienechromium tetracarbonyl under conditions of the reaction produced the same dimers in the same ratios; (c) from Figure 1 one can see that $Cr(CO)_6$ decreases with a concomitant increase in norbornadienechromium tetracarbonyl followed by an increase in dimer concentration.

The typical reaction was run using purified, neat norbornadiene, 0.748 g of $Cr(CO)_6$, and light (2800 Å) emitted from a Hanovia 450-W mercury arc. The reaction was purged for 10 to 12 hr with oxygen-free nitrogen to prevent decomposition of chromium species. From a combination of nmr spectra and vpc retention times the three dimers of norbornadiene, I, II, and III, were identified and found in the ratio of 1.8:1.0:1.4, respectively. To our knowledge this is the first catalyst that produces all three of the known dimers. The overall yield of dimer based on $Cr(CO)_6$ was 40%. Irradiation of neat norbornadiene with no metal present under the same reaction conditions yielded no dimer products. If the reaction is stopped at the maximum concentration of norbornadienechromium tetracarbonyl (about 3 hr) as detected by ir analysis, a 50% yield of this species can be obtained based upon $Cr(CO)_6$ concentration. Norbornadienechromiumtetracarbonyl was identified by melting point and spectral data.

The question arises as to whether or not norbornadienechromium tetracarbonyl arises from thermal reaction from the heat of the lamp or from photochemical reaction. Both thermal[12] and photochemical[13] substitutions have been demonstrated to occur with chromium hexacarbonyl. Bennett, *et al.*,[12] have shown that upon heating $Cr(CO)_6$ with norbornadiene for 2 days at 100-120° a 33% yield of norbornadienechromium tetracarbonyl was obtained. Due to the construction of our photoapparatus which insulates the lamp from the reaction medium with a water-cooled jacket, the temperature in the reaction medium does not exceed 40°. Thus in comparing the reaction conditions of Bennett to ours, it is reasonable to explain the major formation of norbornadienechromium tetracarbonyl by the photochemical process.

Since neither norbornadienechromium tetracarbonyl nor $Cr(CO)_6$ produce any dimeric products on thermal reaction (temperature of our reaction) with norbornadiene, we have further concluded that there are at least two photoprocesses occurring in the $Cr(CO)_6$ reaction: (1) formation of norbornadienechromium tetracarbonyl from $Cr(CO)_6$ and (2) excitation of norbornadienechromium tetracarbonyl for dimerization.[14]

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