Polarized Photochemistry and Photo-orientation of Pentacarbonylchromium in Low-temperature Matrices

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Summary Plane-polarized light has been used to produce oriented $[Cr(CO)_5]$ in CH_4 matrices, the symmetry of the 489 nm transition of $[Cr(CO)_5]$ is determined, and photo-orientation is demonstrated for the first time.

Lewis and his co-workers[1] and, more recently, Albrecht[2] have shown that photolysis with plane-polarized light of a compound randomly oriented in a glass at 77 K can lead to non-randomly oriented photoproducts by preferential photolysis of molecules in particular orientations. However, they were unable to observe any photo-orientation: *i.e.* re-orientation of the photoproducts by light with polarization perpendicular to the original irradiation source. We report evidence for both polarized photochemistry and photo-orientation of matrix-isolated $[Cr(CO)_5]$.

U.v. photolysis of $[Cr(CO)_6]$, isolated in a CH_4 matrix, rapidly generates $[Cr(CO)_5]$ with a C_{4v} square-pyramidal structure.[3]† Subsequent irradiation in the visible band of $[Cr(CO)_5]$ (489 nm, 20,500 cm^{-1}) causes recombination with CO to form $[Cr(CO)_6]$.[4] The Table summarizes the results of

$$[Cr(CO)_6] \underset{489\ \text{nm}}{\overset{\text{U.v.}}{\rightleftharpoons}} [Cr(CO)_5] + CO$$

three experiments in which the recombination was promoted by plane-polarized light and the i.r. and visible spectra of the remaining $[Cr(CO)_5]$ were recorded with polarized light. From the Table we can see: (a) The $[Cr(CO)_5]$ generated by unpolarized u.v. light is randomly oriented since $I_{\parallel}/I_{\perp} =$ *ca.* 1 for all bands.‡ (b) Irradiation with visible light, polarized $\parallel$, 'leaves behind' $[Cr(CO)_5]$, which must be oriented since $I_{\parallel}/I_{\perp}$ $(E) < 1 < I_{\parallel}/I_{\perp}$ (A_1). Similarly $[Cr(CO)_5]$ is oriented by $\perp$ polarized light, but the ratios are inverted. (c) From the intensity ratios it is clear that the

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† Ozin has recently suggested (E. P. Kundig and G. A. Ozin, *J. Amer. Chem. Soc.*, 1974, **96**, 3820) that the most stable form of $[Cr(CO)_5]$ is D_{3h}. It has been shown that this claim is incorrect.[4]

‡ This is not unexpected since the parent $[Cr(CO)_6]$ belongs to a cubic point group. The $I_{\parallel}/I_{\perp}$ ratios for $[Cr(CO)_6]$ should be unity irrespective of orientation and are included in the Table to give an estimate of the experimental errors. The visible intensities are probably the most reliable.

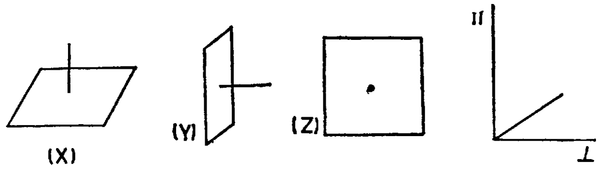
TABLE

Intensity ratio[a] $I_{\parallel}/I_{\perp}$

			$[Cr(CO)_6]$		$[Cr(CO)_5]$				
Polarizer orientation[c]	Symmetry		T_{1u}	T_{1u}	E	A_1	A_1	E	E
	Position in cm^{-1} ..		1985	665	1961	1932	659	647	20,500
	Irradiation time								
U	Expt. 1[b]	15 s	0·97		0·97	1·00			
$\parallel$		5 min	0·91		0·76	1·75			
$\perp$		10 min	0·96		1·20	0·55			
$\parallel$		5 min	1·00		0·82	1·50			
U	Expt. 2[b]	2 min	1·05			1·11			1·00
$\parallel$		21 min				1·35			0·77
$\perp$		15 min				0·78			1·32
$\parallel$		15 min				1·30			0·76
U	Expt. 3[b]	1 min	1·07			1·06			1·01
$\parallel$		6·5 min		1·20		1·19	1·45	0·77	
$\perp$		10 min		1·07		0·89	0·73	1·18	1·19

[a] Ratio of intensities of spectra taken with plane-polarized light with electric vector parallel ($\parallel$) to and perpendicular ($\perp$) to laboratory fixed axes and in direct ion perpendicular to the sample on the low-temperature window. [b] In each experiment the $[Cr(CO)_6]$–CH_4 gas mixture (1 : 5000) was pulsed on to a CsBr window at 20 K. The blanks in the Table occur since it was not possible because of intensity differences to measure the intensity of every band in each experiment. [c] U, Unfiltered, unpolarized Hg arc, $\parallel$; $\lambda > 375$ nm filter, Hg arc plus polarizer $\parallel$; $\perp$, $\lambda > 375$ nm filter, Hg arc plus polarizer $\perp$.

visible transition has the same symmetry, E, as the 1961 cm^{-1} C–O stretching i.r. band, the symmetry of which has been established independently by ^{13}CO substitution.[3] This strongly suggests that the previously proposed assignment[4] for this transition $^1A_1(b_2{}^2e^4) \longrightarrow {}^1E(b_2{}^2e^3a_1{}^1)$ is correct (*i.e.* a transition moment of species E).



Similarly the symmetries of the M–C–O bending vibrations are A_1 (659) and E (647 cm^{-1}), which is consistent with the assignment proposed for $[Mn(CO)_5Br]$.[5]

The effect of polarized light on $[Cr(CO)_5]$ can be understood by considering three extreme orientations of $[Cr(CO)_5]$. Since the light absorption arises from an E transition in the plane of the equatorial CO groups, only molecules Y and Z will interact with $\parallel$ polarized light and molecule X will be unaffected. Thus the ratio X/(Y + Z) increases, the remaining $[Cr(CO)_5]$ is partially oriented, and $I_{\parallel}/I_{\perp}$ (E) < 1. With $\perp$ polarized light, Y is unaffected and the opposite orientation is observed.

The most remarkable aspect of these experiments is illustrated in the Figure. It is clear that irradiation with polarized light not only reduces the amount of $[Cr(CO)_5]$ in one orientation but *increases* the amount of $[Cr(CO)_5]$ in the opposite orientation. Thus the $[Cr(CO)_5]$ molecules are actually being re-oriented in the matrix. With $\parallel$ polarized light this photo-orientation can be imagined as rotation of Y (and Z) to X and with $\perp$ polarized light as rotation of X (and Z) to Y.

This photo-orientation has important implications for understanding the photochemical reactions of $[Cr(CO)_5]$. Recent calculations[6] predict a trigonal bipyramidal, D_{3h}, structure for the excited state of $[Cr(CO)_5]$ which is involved in visible photochemical reactions. This D_{3h} structure could decay back to the C_{4v} ground state in several orientations, producing an apparent rotation. This mechanism could explain a number of observations in matrix

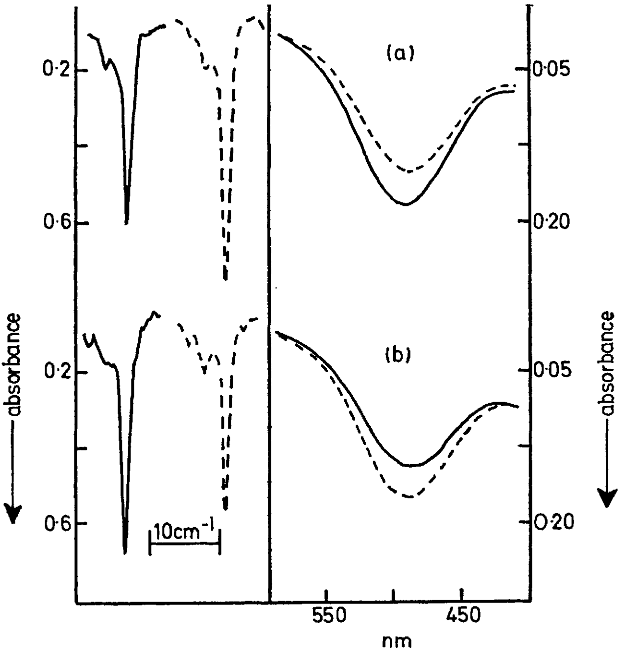


FIGURE. Polarized absorption spectra of $[Cr(CO)_5]$; A_1 C–O stretching vibration (i.r. 1932 cm^{-1}) and electronic transition (489 nm). ———, polarizer $\parallel$; – – –, polarizer $\perp$. Spectra taken after photolysis with $\lambda > 375$ nm (a) 15 min $\perp$; (b) 15 min $\parallel$.

photochemistry, *e.g.* the photochemical regeneration of $[Cr(CO)_6]$ from $[Cr(CO)_5]$, the $[Cr(CO)_5 \cdots Ne]/[Cr(CO)_5 \cdots Xe]$ exchange[4] in mixed Xe–Ne matrices, and the photochemical *cis–trans* isomerization of $[Mo(CO)_4PX_3]$[7] and $[Cr(CO)_4CS]$.[8]

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[2] See *e.g.*, A. C. Albrecht, *J. Mol. Spectroscopy*, **1961**, **6**, 84, references therein.

[3] R. N. Perutz and J. J. Turner, *Inorg. Chem.*, in the press; see also M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc.* (*A*), 1971, 2939.

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