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A Possible Reinterpretation of the Photoelectron Spectra of $[\mathrm{CCl_2}]^{-\bullet}$, $[\mathrm{CBr_2}]^{-\bullet}$, and $[\mathrm{CI_2}]^{-\bullet}$: A Role for Quartet Isodihalocarbene or Dihalocarbene Radical Anions?

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We address a discrepancy between the large singlet−triplet (S−T) splitting values computed by advanced ab initio methods for three of the dihalocarbenes $\mathrm{CX_2}$ (X = Cl, Br, I) and the much smaller values deduced from photoelectron spectra of $\mathrm{CX_2}^{-\bullet}$ ions. Our G3 calculations lead us to propose that the band of $\mathrm{CX_2}^{-\bullet}$ (X = Cl, Br, I) that is presently attributed to the $^2[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$ transition is actually due to photodetachment from a metastable species, $^4[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$ or, less likely, $^4[\mathrm{C{=}X{-}X}]^{-\bullet} \rightarrow {}^3[\mathrm{C{=}X{-}X}]$ (and, conceivably, $^2[\mathrm{C{=}X{-}X}]^{-\bullet} \rightarrow {}^3[\mathrm{C{=}X{-}X}]$).

The singlet−triplet (S−T) splitting in carbenes has long served as a fertile ground for confrontation of theory with experiment. Currently, there is an intolerable[1] discrepancy between the large S−T splitting values computed[2−6] by advanced ab initio methods for three of the dihalocarbenes $\mathrm{CX_2}$ (X = Cl, Br, I) and the much smaller values deduced from photoelectron spectra[7] of $\mathrm{CX_2}^{-\bullet}$ ions (Table 1). We propose a plausible and testable resolution.

The two bands observed in each spectrum have been attributed[7] to electron detachment transitions from the ground doublet state of the radical anion $^2[\mathrm{X{-}C{-}X}]^{-\bullet}$ to the singlet $^1\mathrm{X{-}C{-}X}$ and triplet $^3\mathrm{X{-}C{-}X}$ of the neutral carbene. There is no particular reason to doubt the singlet band assignment, because the resulting adiabatic electron affinities for all four $^1\mathrm{X{-}C{-}X}$ ground states are just those expected from advanced calculations.[5] Nor is there any reason to doubt the triplet band assignment for $\mathrm{CF_2}$[7] or the four related monohalocarbenes CHX,[8] all of which yield S−T values in agreement with theory. Only the triplet bands for $\mathrm{CX_2}$ (X = Cl, Br, I) are strongly displaced relative to theoretical expectations. This is remarkable, considering that all eight ions were produced in similar reactions[9] of $\mathrm{CH_2X_2}$ or $\mathrm{CH_3X}$ with $\mathrm{O}^{-\bullet}$ generated in a $\mathrm{He/O_2}$ microwave discharge and mass selected and that all of the data were handled in the same way. Conceivable sources of experimental error have been suggested.[5] However, the simplest solution of the problem would be to reassign the band of $\mathrm{CX_2}^{-\bullet}$ (X = Cl, Br, I) that is presently attributed to the $^2[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$ transition. If this band were due to photodetachment from a metastable state higher in energy by just the right amount, and if one could explain why this state is populated only in $\mathrm{CX_2}^{-\bullet}$ (X = Cl, Br, I), the mystery would be solved. Likely metastable candidates are the quartet $^4[\mathrm{X{-}C{-}X}]^{-\bullet}$ and the doublet or quartet of the structural isomer $[\mathrm{C{=}X{-}X}]^{-\bullet}$, and we presently examine their viability.

Two aspects of the dihalocarbene results[7] hint in this direction: When X = F, photoelectrons from $\mathrm{CX_2}^{-\bullet}$ have the expected angular distribution (asymmetry parameter $\beta = 2$) and the triplet and singlet bands have comparable intensities at the magic angle of polarization. When X = Cl, Br, or I, β is 0.4−0.5 and triplet bands are much stronger than singlet bands, suggesting that they might correspond to electron detachment from different species.

We have performed a preliminary survey of these structures by the relatively inexpensive G3B3//B3LYP/6-31G(d) (X = F, Cl), G2(ECP(S))//B3LYP/6-31+G(d) (X = Br), and G2(ECP(S))//B3LYP/ECP(S) (X = I) methods[10] (Figure 1 and Table 1). The G3 method is quite reliable for halocarbenes,[4] and results for previously calculated structures agree closely with the best published. We find that (i) a reassignment of the problematic band in $\mathrm{CX_2}^{-\bullet}$ (X = Cl, Br, I) to either the $^4[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$ or the $^4[\mathrm{C{=}X{-}X}]^{-\bullet} \rightarrow {}^3[\mathrm{C{=}X{-}X}]$ photodetachment transition agrees with theory to within a few kcal/mol, (ii) the vertical $^2[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$, $^2[\mathrm{C{=}X{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{C{=}X{-}X}$, $^2[\mathrm{C{=}X{-}X}]^{-\bullet} \rightarrow {}^1\mathrm{C{=}X{-}X}$, and $^4[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^5\mathrm{X{-}C{-}X}$ transitions lie outside of the 0−75 kcal/mol window of observation, while the $^4[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^1\mathrm{X{-}C{-}X}$ transition is forbidden, leaving only two expected bands (the weak origin region of the $^2[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$ transition would be buried under the band of the metastable quartets), and (iii) a plausible mechanism exists for the population of the metastable $^{2,4}[\mathrm{C{=}X{-}X}]^{-\bullet}$ and $^4[\mathrm{X{-}C{-}X}]^{-\bullet}$ states, but only in the three problematic cases.

The comparison with theory is based on vertical excitations, because the determination of experimental adiabatic detachment energies requires a fitting of the Franck−Condon envelope and depends on the structure pair assumed. The fitting will be necessary in the full paper, but we believe that even the present preliminary note may prompt additional experiments. Unlike $^1\mathrm{C{=}X{-}X}$, which corresponds to a local minimum on the singlet potential energy surface and is a metastable isomer of $^1\mathrm{X{-}C{-}X}$, $^3\mathrm{C{=}X{-}X}$ is not separated by a barrier from $^3\mathrm{X{-}C{-}X}$, which is the only stable triplet isomer. The reported adiabatic detachment energies of the triplet bands (Table 1) actually agree very well with the calculated adiabatic detachment energies from $^2[\mathrm{C{=}X{-}X}]^{-\bullet}$ (38, 43, and 45 kcal/mol for X = Cl, Br, and I, respectively), suggesting that the metastable species observed is $^2[\mathrm{C{=}X{-}X}]^{-\bullet}$, but this is perhaps a coincidence because the experimental data were analyzed under the assumption that the detachment process is $^2[\mathrm{X{-}C{-}X}]^{-\bullet} \rightarrow {}^3\mathrm{X{-}C{-}X}$, and the computed vertical energies disagree.

The limitation to a comparison of vertical detachment energies is unfortunate, because the identification of the vertical excitation

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TABLE 1: Electron Detachment Energies[a] of $[X-C-X]^{-\bullet}$ and $[C=X-X]^{-\bullet}$ Ions (kcal/mol)

transition		X = F		X = Cl		X = Br		X = I	
		calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
$^2[X-C-X]^{-\bullet} \rightarrow {}^1[X-C-X]$	vert	23	21	53	50	49	54	58	56
	adiab	4	4	35	37	39	43	48	50
$^2[X-C-X]^{-\bullet} \rightarrow {}^3[X-C-X]$	vert	84	68	89	(62)[b]	84	(65)[b]	85	(65)[b]
	adiab	60	58	56	(39)[b,c]	59	(46)[b,c]	63	(48)[b,c]
$^4[X-C-X]^{-\bullet} \rightarrow {}^3[X-C-X]$	vert	51		65	62	61	65	66	65
$^4[X-C-X]^{-\bullet} \rightarrow {}^5[X-C-X]$	vert	168		136		124		112	
$^2[C=X-X]^{-\bullet} \rightarrow {}^1[C=X-X]$	vert			*d*		107		*d*	
$^2[C=X-X]^{-\bullet} \rightarrow {}^3[C=X-X]$	vert			93		91		87	
$^4[C=X-X]^{-\bullet} \rightarrow {}^3[C=X-X]$	vert			59[e]	62	62	65	68	65
$^4[C=X-X]^{-\bullet} \rightarrow {}^5[C=X-X]$	vert			111[e]		118		117	

[a] Calculated energies: X = F, Cl at G3B3; X = Br at G2(ECP)//B3LYP/6-31G(d); X = I at G2(ECP)//B3LYP/ECP. Observed energies from ref 7. [b] Original assignment, now proposed to be incorrect. [c] Franck−Condon envelope calculation assumed the original assignment, now considered incorrect. [d] QCISD(T) did not converge after 250 iterations. [e] Minimum geometry from a G3B3 reaction coordinate of the $^4[C=X-X]^{-\bullet}$ to $^4[X-C-X]^{-\bullet}$ rearrangement; valence angle ≈ 170°.

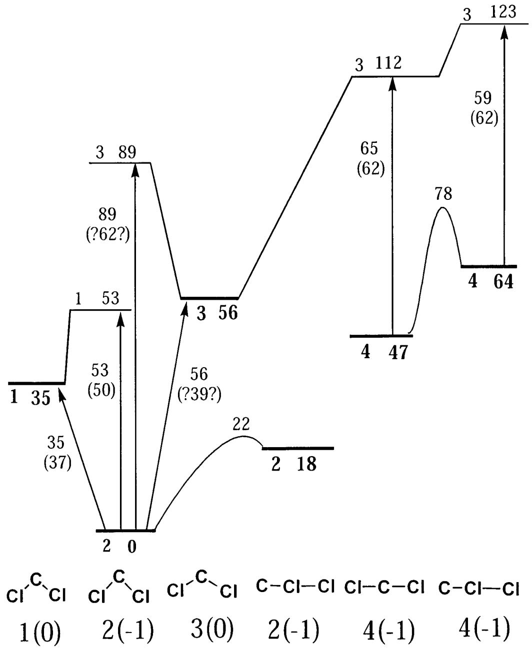

Figure 1. Computed and observed (in parentheses) energies of neutral and charged (charge in parentheses) states of dichlorocarbenes and isochlorocarbenes (multiplicity shown), evaluated at geometries optimized for the species shown at the bottom of each column.

TABLE 2: Energy (E)[a] and Activation Energy ($\Delta E^{\ddagger}$)[b] for Intermediates and Products in $O^{-\bullet}$ + CH_2X_2 Abstraction Reactions (kcal/mol)

	X = Cl				X = Br				X = I			
	^2E	^4E	$^2\Delta E^{\ddagger}$	$^4\Delta E^{\ddagger}$	^2E	^4E	$^2\Delta E^{\ddagger}$	$^4\Delta E^{\ddagger}$	^2E	^4E	$^2\Delta E^{\ddagger}$	$^4\Delta E^{\ddagger}$
$X^{\bullet}CHX$	0	89[c]										
$H^{\bullet}C=XX$	80	87			*d*							
$[X-C-X]^{-\bullet}$	0	47			0	39			0	33		
$[C=X-X]^{-\bullet}$	18	64	5	13	16	54	6	20	18	44	6	17

[a] Adiabatic, relative to $X^{\bullet}CHX$ and $[X-C-X]^{-\bullet}$. [b] Activation energies for the $^2[C=X-X]^{-\bullet} \rightarrow {}^2[X-C-X]^{-\bullet}$ and $^4[C=X-X]^{-\bullet} \rightarrow {}^4[X-C-X]^{-\bullet}$ rearrangements. [c] $^4X^{\bullet}CHX$ dissociates into ^3HCCl and ^2Cl. [d] QCI failed to converge.

energy with the band maximum is only approximate. Indeed, even cases in which there is no reason to doubt the reported assignments and in which the present calculations agree with the observed adiabatic detachment energies within 1−2 kcal/mol (in kcal/mol, for CHF, CHCl, and CF_2, doublet → singlet calcd. 12, 27, and 4, obsd. 13, 28, and 4; doublet → triplet calcd. 27, 33, and 60, obsd. 28, 32, and 58), the agreement for vertical detachment energies, particularly the high ones, is much poorer (doublet → singlet calcd. 22, 43, and 23, obsd. ∼20, ∼35, and ∼21; doublet → triplet calcd. 44, 64, and 84, obsd. ∼37, ∼54, and ∼68). The discrepancy persists at the CCSD(T)/aug-cc-pVTZ level of calculation for $^2[F-C-F]^{-\bullet} \rightarrow {}^3F-C-F$ (calculated adiabatic and vertical electron detachment energies are 56 and 77 kcal/mol, respectively).[11] We believe that it is due to band shape distortion by instrumental discrimination against electrons with very low kinetic energies. While this would have negligible effect on the adiabatic detachment energies, it would produce artificially low vertical detachment energies.

Why would the metastable states be populated only in the three problematic cases? The $CX_2^{-\bullet}$ radical ions are formed[9] by hydrogen atom abstraction from $X-CH_2-X$ by $^2O^{-\bullet}$, producing the hot ion−molecule complex (HO^-, $^{2\bullet}CHX_2$) in which proton transfer takes place to yield $^2CX_2^{-\bullet}$ and H_2O, which ultimately separate. The quartet (Q) state is calculated to be much above the doublet (D) in the reactants, in the $^{\bullet}CHX_2$ intermediate, and in the product, which should therefore be formed in the ground D state, as is usual (Table 2). We propose that metastable quartet formation starts with a photoisomerization of some of the dihalomethane $X-CH_2-X$ to its less stable isomer $CH_2=X-X$ upon UV irradiation, well established[12−15] when X = Cl, Br, or I and not available when X = F and in CH_3X. Because a microwave discharge is an intense source of UV light, it would be surprising if some of the $CH_2=X-X$ isomer did not form. We propose that the isodihalomethanes also undergo the abstraction reaction with $^2O^{-\bullet}$, and yield $[C=X-X]^{-\bullet}$, calculated to be metastable. The calculated adiabatic D−Q splitting in the $^{\bullet}CHX=X$ intermediate is small (Table 2). The initial H atom abstraction is exothermic, the hot (HO^-, $^{2\bullet}CHX=X$) complex is cooled only slowly (in ∼0.5 Torr of He), and the spin−orbit coupling is large (86, 351, and 744 cm^{-1} when X = Cl, Br, and I, respectively),[16] providing an opportunity for D → Q intersystem crossing before the proton transfers and the complex dissociates. After proton transfer, the D−Q splitting is again increased, the rate of intersystem crossing drops exponentially, and $^4[C=X-X]^{-\bullet}$ will be metastable. However, the high-energy isomers, $^2[C=X-X]^{-\bullet}$ and $^4[C=X-X]^{-\bullet}$ (X = Cl, Br, I), could rearrange to the stable isomers, $^2[X-C-X]^{-\bullet}$ and $^4[X-C-X]^{-\bullet}$ (Table 2). The barriers to this rearrangement were calculated for X = Cl and are 5 and 13 kcal/mol, respectively. After isomerization, the D−Q separation is even larger and Q is expected to be long-lived. The vertical detachment energies of both sets of quartet isomers, $^4[C=X-X]^{-\bullet}$ and $^4[X-C-X]^{-\bullet}$, are similar, and both agree with the observed triplet band position. Either or both could be responsible for the observed spectral bands. Because the triplet band peaks are not broadened relative to those of the singlet band and because the only minimum computed for the triplet surface is at ^{3}[X−C−X], ^{4}[X−C−X]$^{-\bullet}$ is the more likely candidate.

The small D−Q splitting in H$^\bullet$C═X−X is the key to the proposed formation of the quartet states. It results from the nature of bonding in this radical, which is H−C−X weakly interacting with an X atom. The D−Q splitting reflects the small observed[8] and calculated[6] S−T splitting in the carbene. In contrast, in X$^\bullet$CHX, the D → Q excitation requires a local S−T excitation of a σ-bonding electron pair and, in [X−C−X]$^{-\bullet}$, a similar excitation of a lone pair electron into a C−X antibonding orbital. The simplest description of ^{2}[C═X−X]$^{-\bullet}$ is ^{2}CX interacting with an X$^-$ anion, and its large D−Q splitting is similar to that in CX (for X = Cl, 55 kcal/mol).

The present proposal is only tentative, but it offers a plausible alternative interpretation of the photoelectron spectra originally attributed solely to dihalocarbene radical anions.[7] It suggests additional experiments to check whether for X = Cl, Br, and I the singlet and triplet bands are indeed due to two distinct species, and it also suggests that additional computations at a higher level of theory will be worthwhile.

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Supporting Information Available: Total energies of dihalocarbenes, isodihalocarbenes, and their radical anions. This material is available free of charge via the Internet at http://pubs.acs.org.

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