characteristic (+ or −) amount Δx, which we assume to be independent of the other substituents. In CHXYZ, the resulting difference in the 2s electron content at the bottom of the wells is $\Delta x + \Delta y + \Delta z$, which must be accommodated by a change in the *common level* at the top of each of the four wells. This, by means of Eq. (7), leads to

$$\Delta x + \Delta y + \Delta z = 4[\alpha_H^2(\mathrm{CHXYZ}) - (1/4)] \quad (8)$$

For monosubstituted derivatives, Eq. (8) reduces to

$$\Delta x = 4[\alpha_H^2(\mathrm{CH_3X}) - (1/4)] \quad (9)$$

which enables us to eliminate Δx, Δy, and Δz from Eq. (8) and obtain

$$\begin{aligned}\alpha_H^2(\mathrm{CHXYZ}) = [\alpha_H^2(\mathrm{CH_3X}) - (2/3)\alpha_H^2(\mathrm{CH_4})] + \\ [\alpha_H^2(\mathrm{CH_3Y}) - (2/3)\alpha_H^2(\mathrm{CH_4})] + \\ [\alpha_H^2(\mathrm{CH_3Z}) - (2/3)\alpha_H^2(\mathrm{CH_4})] \quad (10)\end{aligned}$$

And, finally, the relation between J_{CH} and α_H^2, in Eq. (6), converts this to

$$J_{\mathrm{CH}}(\mathrm{CHXYZ}) = \zeta_X + \zeta_Y + \zeta_Z \quad (11)$$

which is exactly the form of additivity observed by Malinowski.[4] A two-center molecular orbital of the form

$$\psi = c_1(1s_H) + c_2(2s_C) + c_3(2p_{\sigma_C}) \quad (12)$$

yields essentially the same equation as Eq. (6), after which the analysis is identical.

The formalism introduced above enables one to use experimental values of J_{CH} to obtain not only α_H^2 but also α_X^2. The relation of these quantities to parameters such as bond angles and lengths is under investigation and will be reported later[10] along with details of the present work. In addition, it appears that substituent parameters obtained from the monosubstituted methanes can be applied to J_{CH} in substituted ethylenes.

The $\mathrm{Si^{29}}$–H coupling has been observed in $\mathrm{SiH_4}$ and in a number of derivatives.[11] However, our inspection of the results shows that the substituent effects are not additive. Nonetheless, the deviations from additivity are systematic in that for the halosilanes, the deviations follow the sequences: $\mathrm{SiHX_3} > \mathrm{SiH_2X_2}$; and F > Cl > Br > I. Several factors can contribute to these effects, of which the most likely appears to be the use by Si of 3d orbitals, the importance of which is suggested also by the dependence of J_{HH} upon the H–Si–H angle.[11,12] The inclusion of 3d orbitals in Eq. (5) may prevent Eq. (6) from applying to J_{SiH}, and also it could affect Eq. (7). This presents the attractive possibility of learning something about the d hybridization from the deviations, to compensate for the more difficult nature of the analysis.

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[10] C. S. Juan and H. S. Gutowsky, to be submitted to *J. Chem. Phys.*

[11] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, in press; we are indebted to the authors for making their results available to us before publication.

[12] J. C. Schug and H. S. Gutowsky, unpublished results.

THE REACTIONS OF ATOMIC CARBON WITH ETHYLENE[1]

Sir:

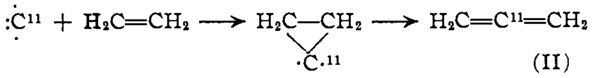
The reactions of atomic carbon with ethylene have been studied. Recoil $\mathrm{C^{11}}$ from a nuclear reaction was introduced into the gaseous reagent, and analysis made for the $\mathrm{C^{11}}$-labeled radioactive products by techniques outlined previously.[2] Results are summarized in Table I. Column I shows products obtained with pure ethylene, column II with oxygen added as a radical scavenger, and column III is representative of runs containing a large excess of neon to thermalize (*i.e.*, remove excess kinetic energy from) the carbon atom before reaction.

As with the alkanes previously reported,[2] the main products are highly unsaturated hydrocarbons. The high yield of acetylene, in particular, probably results largely from the C–H bond insertion process as postulated for the alkanes.

$$\cdot\ddot{\mathrm{C}}\cdot^{11} + \mathrm{H_2C{=}CH_2} \rightarrow \dot{\mathrm{C}}\mathrm{H_2} + \mathrm{HC^{11}{\equiv}CH} \quad \text{(I)}$$

However, there are two significant differences between ethylenic hydrocarbons in general and saturated systems: (1) in the presence of $\mathrm{O_2}$ the CO yield is appreciably less with alkenes than with alkanes. This indicates the alkenes are more reactive. (2) The yields of products containing one more carbon atom than the reacting hydrocarbon are considerably higher with alkenes than with alkanes. Thus about twice as much allene and methylacetylene form from ethylene, as do propane and propylene from ethane.

The most obvious and satisfactory explanation of these observations is that the C atom can react directly with the double bond to form a π-bonded species. This intermediate then can rearrange to allene[3]



$$:\!\dot{\underset{\cdot}{\mathrm{C}}}{}^{11} + \mathrm{H_2C{=}CH_2} \longrightarrow \underset{\cdot\mathrm{C}\cdot^{11}}{\mathrm{H_2C{-}CH_2}} \longrightarrow \mathrm{H_2C{=}C^{11}{=}CH_2} \quad \text{(II)}$$

(In the case of higher alkenes, the corresponding substituted allene largely isomerizes to a conjugated diene.) We are presently attempting to confirm this mechanism by showing that $\mathrm{C^{11}}$ appears in the central position of allene.[4]

The intermediate formed by this double bond addition also has sufficient energy to decompose with bond rupture. It may thus contribute to the yield of acetylene-$\mathrm{C^{11}}$ from ethylene.

The cyclopropane observed is consistent with the previous hypothesis that a few per cent of the C atoms react by H atom pick-up from hydrocarbons[2] to form $\mathrm{C^{11}H_2}$. This will react in a characteristic

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[2] C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2399 (1961).

[3] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

[4] Note that a certain amount of allene with terminal $\mathrm{C^{11}}$, resulting from the C–H bond insertion mechanism (see ref. 2), also may be expected.

TABLE I

C^{11} LABELED PRODUCTS OF REACTION OF ATOMIC C^{11} WITH ETHYLENE YIELDS AS % OF TOTAL GASEOUS ACTIVITY

Each yield represents the average of at least three runs. Errors indicated are a measure of reproducibility. C_4 or lighter hydrocarbons not mentioned <1% (or <5% for moderated runs.)

	Composition of reacting gas (Total press. 1 atm)		
C^{11} Product	C_2H_4	C_2H_4 (98.5%) O_2 (1.5%)	C_2H_4 (4.5%) O_2 (0.2%) Ne (95.3%)
Carbon monoxide[a]	0.9 ± 0.3	9.8 ± 2.0	24 ± 5
Ethylene	1.5 ± 0.5	2.0 ± 1.0	...
Acetylene	38.0 ± 3.5	36.6 ± 1.5	31 ± 5
Cyclopropane	3.2 ± 0.7	<1	...
Propylene	3.7 ± 0.6	4.7 ± 0.5[b]	...
Allene	18.0 ± 2.0	15.3 ± 0.8	17 ± 4
Methylacetylene	4.0 ± 1.5	3.7 ± 1.0	...
Vinylacetylene	11.2 ± 1.5	10.6 ± 3.5	...

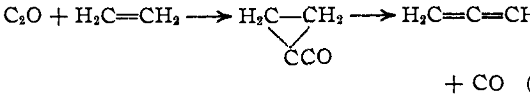
[a] These values may include a small yield of methane. [b] Probably includes an indeterminate amount of CO_2

manner[5] to form cyclopropane-C^{11}. The vinylacetylene found presumably results from the secondary reaction of a two carbon fragment, possibly CC^{11}, formed by decomposition of an excited complex resulting from C–H or C=C insertion.

Column III indicates that the major products obtained from atomic carbon thermalized by neon moderator, are qualitatively similar to those from high kinetic energy carbon. Furthermore, thermalization does not significantly change the relative yield of allene to acetylene. This has been verified by a detailed analysis using the kinetic theory of hot atom reactions,[6] on data from ethylene runs containing various fractions of neon, helium or xenon moderator. Apparently the chemical potential and reactivity of thermal atomic carbon are so high that the addition of kinetic energy makes little, if any, difference to the modes by which it can become chemically combined. In this respect it differs markedly from atomic hydrogen.[6,7] It should be noted, however, that the reaction probability of carbon with ethylene relative to that with oxygen, appears lower at thermal energies.

In a recent communication Bayes[8] reported that the photolysis of C_3O_2 at 2537 Å., in the presence of ethylene, yields allene and carbon monoxide. It was suggested that the C_3O_2 may be dissociated into CO and atomic carbon which reacted to form the allene. This hypothesis was inconsistent with our results that reaction of atomic carbon with ethylene yields acetylene and other major products, as well as allene. Furthermore, we find that addition of small amounts of oxygen increases the CO yield, whereas Bayes' system was unaffected by 18% O_2. Bayes suggested two possible reasons for the discrepancy[8]: (1) that the reactions observed by us were characteristic of hot, but not of thermal, carbon atoms; (2) that the reactive species produced in the photolysis of C_3O_2 was actually C_2O instead of C.

With factor (1) being excluded by our results with neon moderator, it can be concluded that C_2O is the active species produced by photolysis of C_3O_2.[9] Apparently C_2O adds to double bond in a manner similar to atomic carbon and C_2H[5].



(III)

However, atomic carbon is a more energetic and less specific reagent undergoing a wider range of reactions and yielding more products.

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[5] W. von E. Doering, *et al.*, *J. Am. Chem. Soc.*, **78**, 3224 (1956); H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

[6] P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2665 (1960).

[7] D. Urch and R. Wolfgang, *J. Am. Chem. Soc.*, **83**, 2982 (1961).

[8] K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(9) The production of C_2O rather than C by photolysis of C_3O_2 with 2537 Å. radiation also seems more likely on the basis of energy considerations. The heat of formation of C_3O_2 can be estimated, using bond strengths determined from bond length and force constant data [see for example A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947), and L. H. Long and A. D. Walsh, *ibid.*, **43**, 342 (1947)], as not less than about 690 kcal. On this basis the reaction $C_3O_2 \rightarrow C + 2CO$ is endothermic by about 175 kcal. or more, even if the C atom is produced in the triplet ground state in violation of the spin conservation rule. The 2537 Å. radiation supplies only 112 kcal.

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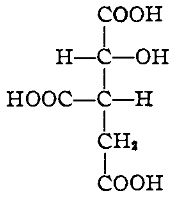
RECEIVED OCTOBER 28, 1961

THE ABSOLUTE CONFIGURATION OF NATURALLY OCCURRING ISOCITRIC ACID[1]

Sir:

In a recent communication from this laboratory[2] a structure determination was reported of the isomorphous monopotassium and monorubidium salts of the lactone of *d*-isocitric acid prepared for us from the Crassulacean plant *Bryophyllum calycinum* by Dr. H. B. Vickery and Dr. D. G. Wilson[3] of the Connecticut Agricultural Experiment Station. From this work we deduced that the configuration of the acid was either D_sL_g isocitric acid (I) or its optical enantiomorph L_sD_g isocitric acid. This



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result was in complete agreement with the work of Gawron[4] and his co-workers who had come to the same conclusion both on physical, chemical and synthetic grounds. Because Greenstein and his

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(1) Work supported by a grant (A2884) from the National Institutes of Health, U. S. Public Health Service. A preliminary account of this work was presented at the Boulder, Colo., meeting of the American Crystallographic Association, August, 1961.

(2) J. P. Glusker, A. L. Patterson, W. E. Love and M. L. Dornberg, *J. Am. Chem. Soc.*, **80**, 4426 (1958).

(3) H. B. Vickery and D. G. Wilson, *J. Biol. Chem.*, **233**, 14 (1958).

(4) (a) O. Gawron and A. J. Glaid, III, *J. Am. Chem. Soc.*, **77**, 6638 (1955); (b) O. Gawron, A. J. Glaid, III, A. LoMonte, and S. Gary, *ibid.*, **80**, 5856 (1958).