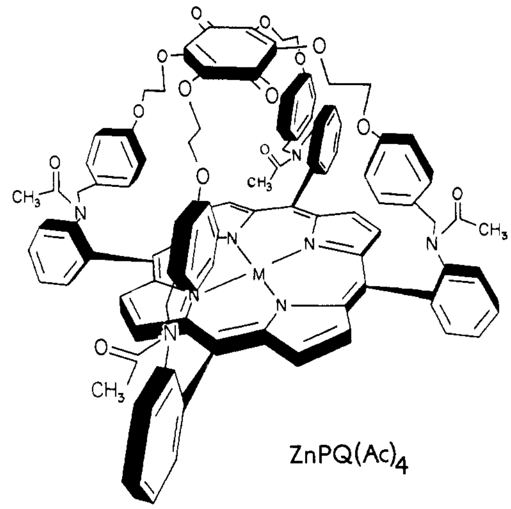

Figure 1. The zinc porphyrin–quinone with the four acetylated aniline groups. The two symmetry axes of the quinone are parallel to and centered above the N–N symmetry axes of the porphyrin.

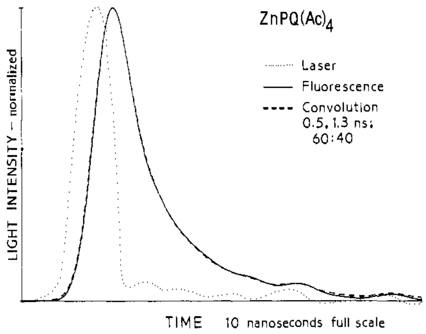

Figure 2. Fluorescence lifetime measurement of $\mathrm{ZnPQ(Ac)_4}$ in acetonitrile at room temperature. A nitrogen laser (PRA Nitromite) was used in conjunction with a Hamamatsu Microchannel 1294 PMT, Tektronix 7912 AD digitizer, and HP 9825A computer. The laser pulse is convoluted with a chosen exponential decay to curve-fit the observed fluorescence decay.

grow in following the flash, with a rise time of 150 ns and a decay time of 1.4 μs. At other wavelengths, particularly at 470 nm where the triplet absorbs strongly, only a fast rise ($\tau < 30$ ns) and subsequent decay, again with $\tau \sim 1.4$ μs, were seen. Since this behavior occurs only with the quinone derivative, we assign this species to the P^+Q^- charge-separated state. The porphyrin cation radical of $\mathrm{ZnPQ(Ac)_4}$ was prepared by $\mathrm{Fe(ClO_4)_3}$ oxidation in acetonitrile and its spectrum generally agreed with the observed flash transient. However, the breadth of both the porphyrin triplet and cation spectra and their apparent close similarity make it difficult to distinguish these species by their absorption.[8] Nevertheless, we may take the constant recovery time found at all wavelengths, in regions both of transient absorption and reversible bleaching, to indicate conversion of the triplet to a single intermediate with lifetime $\tau \sim 1.4$ μs, corresponding to that seen to develop at 415 nm. The rate of transient growth and absence of long-lived decay indicate that the porphyrin triplet state is the progenitor of the charge-separated state, and all of the triplets undergo electron transfer. No very short-lived flash transients were observed over the wavelength interval examined (370–650 nm), indicating that the lifetime of a possibly distinguishable singlet charge-transfer state must be less than 30 ns, as determined by the resolving time of the flash apparatus.

The short triplet lifetime was verified by measurement of delayed fluorescence. The triplet state in both ZnPQ and $\mathrm{ZnPQ(Ac)_4}$ was quenched over 100-fold at 100 μs in comparison with that of $\mathrm{ZnPA_4}$ and $\mathrm{ZnPA_4(Ac)_4}$. Further and absolute proof of the charge-separated state was obtained by measuring the change in ionic conductivity on charge exchange with another metalloporphyrin and on protonation of the semiquinone radical anion.[9]

We estimate the quantum yield of the charge-separated state observed in the flash experiments to be about 30%, based on measurements of flash energy absorbed and cation formed. The total yield of electron transfer is much greater if the quenching of the singlet state also gives a charge-separated state. Thus the electron-transfer processes in $\mathrm{ZnPQ(Ac)_4}$ occur in high yield. Both the singlet- and triplet-state reactions are quantitatively reversible. The rate constant of electron transfer estimated from the fluorescence lifetimes of $\mathrm{ZnPQ(Ac)_4}$ is only 3 times less than that for electron transfer from bacteriopheophytin to ubiquinone in the bacterial reaction center. These components are separated by an estimated 9–12 Å in the reaction center.[2]

The existence of two fluorescence lifetimes in $\mathrm{ZnPQ(Ac)_4}$ suggests that two states may be involved in the singlet charge-transfer process. An intriguing possibility is that the two states correspond to electron occupation of the two closely spaced LUMO's of the porphyrin, which differ by a 90° rotation of the porphyrin symmetry axis.[10]

We may conclude that electronic interactions in the excited state are extensive at distances much greater than the sum of the van der Waals radii of the reacting molecules. Charge-transfer processes in solution must be reconsidered with this in mind.[1,11]

Acknowledgment. This research was supported by The Rockefeller University Graduate Program, grants to The Rockefeller University from the NIH (GM 25693) and the NSF (PCM 8011485), and a grant to Brandeis University from the DOE (Contract AC02-76ERO3117).

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[8] The effects of ortho substitution in the porphyrin cation spectra have been noted previously. See: Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451–3459.

[9] Lindsey, J. S.; Ballard, S. G., manuscript in preparation.

[10] Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138–163.

[11] Mauzerall, D. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Part C, pp 29–52. Miller, J. R. *J. Phys. Chem.* **1975**, *79*, 1070–1078.

Heterogeneous Gas-Phase Ethylation of Methane with Ethylene over Solid Superacids. A ^{13}C Isotope Tracer Study [1]

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The acid-catalyzed alkylation of methane with the lower alkenes is known to be thermodynamically favorable (see Table I),[2] especially at lower temperatures where unfavorable entropy effects are less important. As to date the alkylation of methane with olefins has been carried out under liquid superacid-catalyzed conditions in 'closed' or pressurized flow systems.[3,4] These systems are rather complex due to the ready competing oligomerization

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[1] Electrophilic Reactions at Single Bonds. 18. For part 17, see: Olah, G. A.; Germain, A.; Lin, H. C.; Forsyth, D. C. *J. Am. Chem. Soc.* **1975**, *97*, 2928.

[2] Data derived from: Benson, S. W. "Thermochemical Kinetics"; Wiley-Interscience: New York, 1976. Also quoted in ref 3.

[3] Siskin, M.; Schlosberg, H.; Kocsi, W. P. in "New Strong Acid Catalyzed Alkylation and Reduction Reactions"; Albright, L. F., Goldshy, A. R., Eds.; American Chemical Society: Washington, DC, 1977; No. 55. Siskin, M. *J. Am. Chem. Soc.* **1976**, *98*, 5413.

[4] Sommer, J.; Muller, M.; Laali, K. *Nov. J. Chim.* **1982**, *1*, 3.

Table I. Thermodynamics of Methane Alkylations

reaction	ΔG, kcal/mol 300 K	400 K	500 K
$CH_4 + C_2H_4 \rightarrow C_3H_8$	−9.7	−6.4	−3.2
$CH_4 + C_3H_6 \rightarrow i\text{-}C_4H_{10}$	−7.8	−4.0	−0.3

Table II. Ethylation of $^{13}CH_4$ with C_2H_4[a]

			products normalized,[c,d] %				label content of C_3 fraction,[e] %	
run	$^{13}CH_4$:C_2H_4	catalyst[b]	C_2H_6	C_3H_8	$i\text{-}C_4H_{10}$	C_2H_5F	$^{13}CC_2H_8$	C_3H_8
1	98.7:1.3	TaF_5/AlF_3	51.9	9.9	38.2		31	69
2	99.1:0.9	TaF_5		15.5	3.0	81.5	91	9
3	99.1:0.9	SbF_5/graphite	64.1	31.5		4.4	96	4

[a] All values reported are in mole percentage. [b] Catalysts pretreated with HF for 30 s. [c] Excluding methane. [d] Trace amounts of $(CH_3)_2SiF_2$ detected in all runs are probably due to SiF_4 impurity from HF reacting with methane. [e] Isobutane contained no ^{13}C label, thus it is derived from ethylene.

of olefins. These experiments are also not appealing from a practical point of view due to the severity of the conditions required and the lack of product selectivity. In order to circumvent these problems we have studied the heterogeneous gas-phase alkylation of methane with ethylene under extremely mild conditions over solid superacids.[5] Some of the solid superacidic catalysts used in these experiments were SbF_5 intercalated into graphite, TaF_5 on AlF_3, and TaF_5, respectively, activated by HF.

In order to assess the results of the methane–ethylene reaction over the solid superacids, it is essential to clearly distinguish this process from ethylene oligomerization–cracking processes which readily occur under the same reaction conditions leading to similar products.[6] It should also be stressed that incipient ethyl fluoroantimonate itself can lead to self-condensation.[7] The ethylene condensation and cracking products[6] (including propane) thus can become the major products and easily confuse results of attempted reactions of the ethyl cation with methane. In order to limit the oligomerizattion of ethylene Siskin[3] and Sommer[4] used large excesses of HF–TaF_5 or HF–SbF_5, respectively, in their solution alkylation of alkanes.

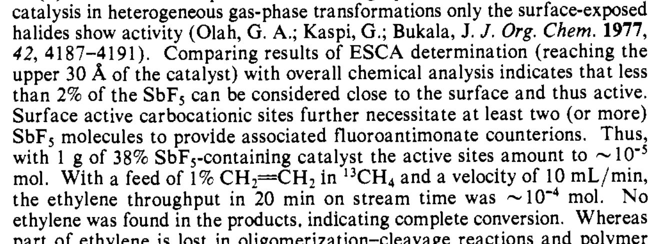
For the reasons outlined it seemed apparent that only labeling experiments (using $^{13}CH_4$) could rigorously distinguish between the methane–ethylene condensation and the ethylene oligomerization reaction. Accordingly we reacted mixtures of excess $^{13}CH_4$ and ethylene over the solid superacid catalysts. In order to minimize side reactions (oligomerization–cleavage), the reactions were performed in a pressurized fixed-bed flow system. The solid superacids (38% SbF_5 intercalated into graphite, TaF_5, and TaF_5–AlF_3 1:1 weight ratio) were pretreated with gaseous HF for 30 s immediately before use. The $^{13}CH_4$–ethylene gas mixture was passed over the solid superacid (generally 1 g) at the rate of 5–10 mL/min at 20–60 psig and ambident temperature in a pressurized system constructed from brass, with an inner Teflon tube reactor 7 cm in length and 0.7 cm in diameter. The gaseous products were collected over a period of 20 min of on-stream time and analyzed for C_1–C_6 products by a Hewlett-Packard 5730A gas chromatograph. The ^{13}C-label content of the propane collected was analyzed by a Hewlett-Packard 5985A gas chromatograph/mass spectrometer. The selective ion monitoring technique (SIM) was employed throughout. It should be noted that $^{13}CH_4$ obtained from the Monsanto Chemical Co. was 99.9% isotopically pure but contained ca. 0.002 mol % propane impurity (triple ^{13}C labeled but free of double or monolabel), which was corrected for in all product analyses. Results are summarized in Table II.

The small-scale experiments (limited by availability of $^{13}CH_4$) did not in general allow accurate determination of turnover numbers and thus to establish the true catalytic nature of the reactions, where the turnover must be >1. (Turnover in heterogeneous catalysis is defined as the number of moles of feed substrate converted per number of catalytic sites.) In case of the SbF_5/grphite-catalyzed reaction, however, such a determination was possible and indicated a turnover of >1.[8]

It can be seen that a significant part (up to 96%) of propane indeed resulted from the methane–ethylene reaction as evidenced by the formation of singly ^{13}C-labeled C_3H_8. The unlabeled propane obtained must have been formed from the ethylene self-condensation–cracking process. Clearly these reactions are in competition with one another and thus should show a dependency on the ethylene concentration. Indeed we found that propane formation is extremely sensitive toward the $^{13}CH_4$–ethylene ratio. Increasing the relative amount of ethylene in the reaction mixture to 2.0 mol % results in a significant decrease of single ^{13}C-labeled propane. In experiments with higher concentrations of ethylene (up to 8.0 mol %) no ^{13}C label is found in any of the products.

Mono-^{13}C-labeled propane can arise only from the acid-catalyzed methane–ethylene condensation reaction.

Mechanistically ethylation of methane is considered to be initiated by protonation of the alkene (ethylene) to form a very reactive incipient ethyl cation, which then inserts into methane via a pentacoordinate carbocation **1** yielding singly labeled propane. In no experiments was there any methyl fluoride observed, nor did pure methane give under the reaction conditions methyl fluoride or any condensation products. Thus the ethylation of methane is clearly catalytic and ^{13}C-mono-labeled propane can come only from the methane–ethylene reaction. The proposed mechanism seems to be the only one in accordance with the experimental results and clearly resembles the solution alkylation mechanism proposed previously.[3,8]



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(5) U. S. and foreign patents applied for.

(6) Pines, H. "The Chemistry of Catalytic Hydrocarbon Conversions"; Academic Press: New York, 1981.

(7) (a) Olah, G. A.; DeMember, J. R.; Schlosberg, R. H.; Halpern, Y. *J. Am. Chem. Soc.* **1972**, *94*, 156. (b) Siskin, M. *Tetrahedron Lett.* **1978**, 527.

(8) As shown in our previous studies of graphite-intercalated metal halide catalysis in heterogeneous gas-phase transformations only the surface-exposed halides show activity (Olah, G. A.; Kaspi, G.; Bukala, J. *J. Org. Chem.* **1977**, *42*, 4187–4191). Comparing results of ESCA determination (reaching the upper 30 Å of the catalyst) with overall chemical analysis indicates that less than 2% of the SbF_5 can be considered close to the surface and thus active. Surface active carbocationic sites further necessitate at least two (or more) SbF_5 molecules to provide associated fluoroantimonate counterions. Thus, with 1 g of 38% SbF_5-containing catalyst the active sites amount to $\sim 10^{-5}$ mol. With a feed of 1% CH_2=CH_2 in $^{13}CH_4$ and a velocity of 10 mL/min, the ethylene throughput in 20 min on stream time was $\sim 10^{-4}$ mol. No ethylene was found in the products, indicating complete conversion. Whereas part of ethylene is lost in oligomerization–cleavage reactions and polymer formation which eventually deactivates the catalyst, the turnover of the methane ethylation is >1, and the reaction is thus catalytic.

In the experiments performed, varying amounts of ethane and ethyl fluoride were also observed. The addition of HF activator to ethylene would explain the formation of ethyl fluoride. Ethane can be produced from the self-condensation of ethylene or from ethyl fluoride. When $^{13}CH_4$ and ethyl fluoride were passed over the TaF_5/AlF_3 catalyst (1:1 weight ratio), ethane constituted up to 7.0 mol % of the products and contained no ^{13}C label.

In conclusion we have demonstrated through ^{13}C isotope labeling studies that methane is ethylated by ethylene to give propane over solid superacid catalysts. A very low concentration of ethylene compared to methane is necessary in order to minimize the self-condensation–cracking of ethylene, which is increasingly becoming the predominant reaction at ethylene concentrations above 1.0 mol %. The reported ethylation of methane is fundamental as the prototype of alkylation of the parent alkane.

Registry No. 1, 32555-23-0; $CH_2{=}CH_2$, 74-85-1; CH_4, 74-82-8; $CH_3CH_2^+$, 14936-94-8; TaF_5, 7783-71-3; AlF_3, 7784-18-1; SbF_5 compound with graphite, 59839-60-0.

Additions and Corrections

Studies of the Tautomerism of Purine and the Protonation of Purine and Its 7- and 9-Methyl Derivatives by Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy [*J. Am. Chem. Soc.* **1982**, *104*, 3162–3164]. NINA C. GONNELLA and JOHN D. ROBERTS*

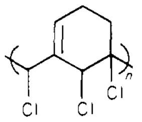
Page 3162: It has been pointed out to us by Prof. Günther (Siegen) that the ^{15}N chemical shift given in Table I for N9 of 9-methylpurine is inconsistent with Figure 3. The value in Table I should be 224.1 ppm rather than 244.1 ppm.

Two Syntheses of *d,l*-Aplysistatin [*J. Am. Chem. Soc.* **1982**, *104*, 6704]. T. R. HOYE,* A. J. CARUSO, J. F. DELLARIA, JR., and M. J. KURTH

Page 6708, left column, lines 23 and 24: The ^1H NMR data for *d,l*-12-epiaplysistatin should read δ 0.94, 1.19, and 1.42 (3 s, 3 CH_3)....

Poly(1,6-heptadiyne), a Free-Standing Polymer Film Dopable to High Electrical Conductivity [*J. Am. Chem. Soc.* **1983**, *105*, 4417–4431]. HARRY W. GIBSON,* F. C. BAILEY, ARTHUR J. EPSTEIN, HEIKO ROMMELMANN, SAMUEL KAPLAN, JOHN HARBOUR, XIAO-QUING YANG, DAVID B. TANNER, and JOHN M. POCHAN

Page 4421, column 1: Structure **17** should be as follows



Page 4421, column 2, paragraph 3, line 5: **19d** and **19f** should be **19d** and **19e**.

Page 4421, column 2, paragraph 3, line 6: **19e** should be **19f**.

Substituent Effects on Benzyl Radical ESR Hyperfine Coupling Constants. The $\sigma_{\alpha}\cdot$ Scale Based upon Spin Delocalization [*J. Am. Chem. Soc.* **1983**, *105*, 1221]. J. M. DUST and D. R. ARNOLD*

Page 1221: The benzyl radical hyperfine coupling constants, listed in Table I, have been redetermined under improved conditions. In several cases the variation is significant enough that revision of Table I (and consequently Tables III and V) is necessary. The interpretative discussion is largely unaffected by these changes. Note, however, that the order of delocalization by 4-*tert*-butyl and 4-methyl are reversed, and the correlation of the logarithm of the rates for the methylenearylcyclopropane rearrangement is better (r = 0.96) vs. $\sigma_{\alpha}\cdot$ alone.

We wish to acknowledge the contribution of D. D. M. Wayner.

Table I. Benzyl Radical Hyperfine Coupling Constants[a] (revised)

X	a_1	a_2	a_3	a_4	a_5	a_6	$\sigma_{\alpha}\cdot$[b]
4-COMe	15.28	5.00	1.75	0.50^{c}	1.75	5.00	0.060
4-COPh	15.35	4.98	1.76		1.76	4.98	0.055
4-COOMe	15.55	5.05	1.75	0.37^{c}	1.75	5.05	0.043
4-CN	15.60	5.00	1.78	0.96^{d}	1.78	5.00	0.040
4-OMe	15.95	5.02	1.60	0.75^{c}	1.60	5.02	0.018
4-SOMe	15.95	5.03	1.75	0.35^{c}	1.75	5.03	0.018
4-Me	16.00	5.05	1.60	6.50^{c}	1.60	5.05	0.015
4-SO_3Me	16.04	5.03	1.71		1.71	5.03	0.013
4-Cl	16.07	5.24	1.75	0.50^{e} 0.60^{e}	1.75	5.24	0.011
4-t-Bu	16.12	5.10	1.75		1.75	5.10	0.008
3-Me	16.22	5.15	3.38^{c}	6.15	1.75	5.00	0.002
H	16.25	5.10	1.70	6.13	1.70	5.10	0.000
3-OPh	16.29	5.15		6.15	1.75	5.00	−0.002
4-OCOMe	16.33	5.27	1.80		1.80	5.27	−0.005
3-Cl	16.37	5.15		6.33	1.83	5.05	−0.007
3-F	16.39	5.15	4.72^{f}	6.19	1.80	4.95	−0.009
4-CF_3	16.39	5.19	1.76	6.88^{g}	1.76	5.19	−0.009
4-F	16.42	5.30	1.75	14.43^{f}	1.75	5.30	−0.011
3-COOMe	16.48	5.22		6.15	1.75	4.98	−0.014
3-CF_3	16.53	5.18	3.30^{g}	6.13	1.80	4.38	−0.017
3-CN	16.68	5.25	0.30^{d}	6.18	1.80	4.95	−0.026

[a] Positions given in Chart I. X is the substituent. Values are believed to be accurate +/− 0.03 G. [b] Defined by eq 1. [c] Hydrogen of CH_3. [d] Nitrogen of CN. [e] Cl. [f] F. [g] Fluorine of CF_3.