TECHNICAL COMMENTS

Triethylsilyl Cations

In their recent report (*1*) about the crystal structure of the compound

$$(C_2H_5)_3Si^+(C_6H_5)_4B^-(C_6H_5CH_3)_2$$

J. B. Lambert *et al.* conclude that the silyl cation is essentially isolated and that the Si atom forms only three bonds (to C atoms of the ethyl groups). Analysis of the values of interatomic distances and bond angles on the basis of structural principles (*2*), however, indicates that there is a fourth bond of significant strength to the para C atom of an adjacent toluene molecule and that a good fraction (35%) of the positive charge of the cation is transferred to the toluene molecule.

The reported distance (*1*) between the Si atom and the para C atom of the toluene molecule is 2.18 Å, which is 0.24 Å greater than the sum of the single-bond covalent radii of C (0.77 Å) and Si (1.17 Å) (*2*, p. 224). The sum of these radii, 1.94 Å, agrees well with the Si-C distances observed in silicon carbide and compounds of Si and the tertiary butyl radical, but smaller values result from hyperconjugation (*2*, pp. 308–309) involving hydrogen atoms attached to the α C atom; there is a decrease of roughly 0.03 Å for each hydrogen atom: 1.91 Å for isopropyl, 1.88 Å for ethyl, and 1.85 Å for methyl. A single covalent bond from Si to C_4 of toluene (with only hydrogen atom attached) would have a length of 1.91 Å; the observed value is 2.18 Å, which is 0.27 Å greater. With use of the well-established equation (*2*, p. 255)

$$D(n) = D(1) - 0.60 \log n$$

this difference leads to $n = 0.35$ for the bond number.

Lambert *et al.* state that the observed Si-C bond length to C_4 of the toluene molecule is so much greater than the single-bond covalent value that one can conclude that this bond, if it is present at all, is very weak. The value $n = 0.35$ found by application of the bond length equation does not correspond to this description. It has been my experience that calculated bond numbers as small as 0.10 (which represent an increase of bond length as great as 0.60 Å) need to be taken into consideration.

Some support for a large value of n is provided by the observed values of the C-Si-C angle of the pyramidal $Si(C_2H_5)_3$ group, 114°, and the height of the Si atom above the plane of the three α C atoms, 0.4 Å. Both of these values are closer to those for tetrahedral Si than to those for a planar group, which suggests a value of n greater than 0.5.

For $n = 0.35$, the expected distortions of the toluene C_6 ring are only about 0.02 Å (*1*, p. 237) and accordingly are difficult to detect.

It is my conclusion, contrary to that of Lambert *et al.*, that the positive electric charge of the silyl cation is not essentially restricted to this cation in this crystal, but is instead (to the extent of about 35%) distributed also over the atoms of the adjacent toluene molecule.

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J. B. Lambert *et al.* report (*1*) the crystal structure of triethylsilyl tetrakis(pentafluorophenyl)borate prepared from toluene solution, and they characterize it as being a somewhat nonplanar triethylsilicenium ion with a noncoordinating anion and as having only distant, weak coordination with toluene, which is incorporated in the crystal lattice. Lambert *et al.* ascertain that the observed 2.18 Å distance between Si and para C of toluene is too long for σ-bonding interaction, and they suggest that the observed nonplanarity of the free triethylsilicenium ion results from weak interaction with toluene, which causes distortion. However, if the triethylsilicenium ion could exist as a long-lived species, it is inconceivable that it could not react with toluene (a good π-base). To probe this question, we repeated the work of Lambert *et al.* and obtained their reported ionic complex. When the complex was quenched with a hindered base besides hexaethyldisiloxane, we then obtained triethylsilyltoluenes, albeit in low (7%) yield. This result is in accord with the formation of the intermediate triethylsilyltoluenium ion which, on competing deprotonation with desilylation, gives the silylated toluenes. Subsequently, we have fully optimized the geometry of the *p*-triethylsilyltoluenium ion (Fig. 1) with the use of the Gaussian-92 series of programs at the HF/6-31G* level, and we calculated its structural parameters and the expected ^{29}Si chemical shift with the use of the IGLO method (*2*).

The calculated bond lengths (Å) and bond angles (Fig. 1) agree well with the reported (*1*) experimental crystal structure data. Whereas the calculations (Fig. 1) refer to gas phase ions, close agreement was found between calculated and observed (carbocation chemistry) structures. Compared to toluene itself, σ-complexed toluene in the crystal structure was clearly deformed. The Si-C4 bond length of 2.18 Å (experimental) and 2.197 Å (theoretical) in the Wheland complex, as compared with a normal Si-C covalent bond distance of 1.85 Å, could be explained by the contribution of β-silicon hyperconjugation.

In the search for stable, long-lived carbocations, differentiation of de facto alkyl cations from polarized donor-acceptor complexes has been possible primarily through study of the involved carbocationic carbon centers with the use of ^{13}C nuclear magnetic resonance (NMR) (*3*). Similar consideration is also valid for trialkylsilyl cations. An R_3Si^+ ion should show very highly deshielded ^{29}Si resonance. Theoretical calculations of the ^{29}Si NMR shift for the still elusive $(CH_3)_3Si^+$ gave a highly deshielded value of $\delta^{29}Si$ 355.7. We calculated with the IGLO II" method at the level of HF/6-31G* (*4*) the ^{29}Si shift of 82.1 ppm for the ion (Fig. 1); the result agreed well with the reported experimental shift of 81.8 ppm (*5*). The ^{29}Si chemical shift of 92.3 ppm in benzene (as opposed to 81.8 ppm in toluene) reflected the weaker π-basicity of the former. When *m*-xylene and mesitylene (which are more basic) were used, the ^{29}Si chemical shift became more shielded at 75.9 and 64.5 ppm, respectively, in accord with the expected trend in silylated arenium ions. For Et_3Si^+ (planar), $\delta^{29}Si$ was calculated to be 354.6. Lambert *et al.* (*1*) suggest that the silyl cation distorts from planarity to relieve external sources of strain and that this leads to the observed large shielding. We have calculated with the IGLO II method at the level of HF/6-31G* the ^{29}Si NMR chemical shift of distorted trimethylsilicenium ion with a C-Si-C angle (a) of 114.00 and 109.47°. We found, however, that they were even more deshielded at 368.2 and 397.0 ppm, respectively, compared to $\delta^{29}Si$ 355.7 for the planar ion (*4*). Thus the experimental shift of 81.8 ppm cannot be that of an Et_3Si^+ species.

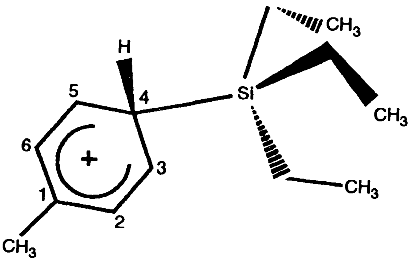

Fig. 1. Schema of the *p*-triethylsilyltoluenium ion. Calculated bond lengths (Å) and bond angles (in parentheses) are Si-C4, 2.197 (2.18); C3-C4, 1.424 (1.40); C2-C3, 1.370 (1.37); C1-C2, 1.403 (1.38) C3-C4-C5, 117.2 (118); EtSiEt, 113.8 (114), Si-C4-C1, 110.3; and H-C4-C1, 157.9

Reed *et al.* recently reported (6) the x-ray structure of the triisopropylsilyl species i-$Pr_3Si(Br_6CB_{11}H_6)$, where the brominated carborane $Br_6CB_{11}H_{6-}$ obtained was considered to be the least nucleophilic anion now known, indicating the highest degree of silylium ion character (R_3Si^+) yet observed. Consideration of the x-ray structure (with Si-Br bond distance of 2.479Å) and the relevant ^{29}Si NMR shift of 109.8 ppm indicate however, that no R_3Si^+ species was observed, but one in which a single bromine atom was silylated, which resulted in a polarized silylbromonium zwitterion. Apparently, this zwitterionic complex was so stable that it did not even react with the toluene from which it was isolated. A R_3Si^+ species with the "highest degree of silylium cation character . . . yet observed" (6, p. 402) could not display such behavior.

Previously we have called attention (4) to pitfalls with regard to reports of observation, and even of isolation, of "free" long-lived R_3Si^+ ions or species with a high degree of R_3Si^+ character that involves "nonnucleophilic" (or "least nucleophilic") anions and aromatic solvents. Toluene and related π-aromatic hydrocarbons (not unlike *n*-coordinating solvents such as sulfones, ethers, nitriles, ketones, and halogenated systems) are unsuitable for use in obtaining long-lived trivalent tricoordinated silicenium cations; they give instead tetracoordinated siylated onium ions (or zwitterions). Lambert *et al.* (1) and Reed *et al.* (6) report significant new results and reliable x-ray structures of isolated silylated ionic complexes. However, both groups incorrectly assign their structures to R_3Si^+ species (free or closely approaching them). It is not thermodynamic, but kinetic instability in all known condensed phase systems that still renders long-lived trialkylsilyl cations elusive.

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Response: We are in essential agreement with Pauling's calculation and do not believe that it is in contradiction with our own conclusions (1). In our report (contrary to Pauling's description of it), we were careful to make no claim for a "tricoordinate," "free," or "three-bonded" silyl cation. Instead, our title emphasized that there was "distant coordination to solvent" and elsewhere that there was "weakly coordinating toluene" at the fourth coordination site. The unprecedented, long Si-C distance between Et_3Si and toluene and the planarity of toluene in an η_1 situation indicate that there is only weak coordination between Si and toluene. We attributed the nonplanarity of the triethylsilyl grouping to this interaction. Pauling provides a quantitative expression for what we described as distant or weak coordination. The energetics of this interaction, as we more recently have determined experimentally, are more akin to noncovalent interactions such as H bonds or electrostatic attractions.

We take minor issue only with the bond distance Pauling uses for $D(1.0)$, which he derived from the sum of the Si and C covalent radii of 1.94 Å (2). Actual experimental measurements of C-Si bond lengths in unstrained structures yield a range of about 1.81 to 1.87 Å, with a mean of 1.845 Å from 20 values (3). Long bonds (1.92 to 2.03 Å) have been found only when there are extremely large substituents around Si or C (3), which is not the case for the triethylsilylium-toluene system. The longest previously measured Si-C bond length, to our knowledge, is 2.03 Å in the extremely crowded four-membered ring [-(*t*-Bu)$_2$Si-(*t*-Bu)$_2$Si-O-CPh$_2$-] (4), hence our use of the descriptor "unprecedented" for the distance between Et_3Si and toluene.

It is the increase from the normal value of C-Si of about 1.85 Å to the observed value of 2.18 Å that provides the appropriate measure of silyl cation character. If the more likely value for $D(1.0)$ of 1.85 Å is used in Pauling's equation, then the calculated value of n is 0.28. Thus the structure has 65 to 72% silylium ion character and is properly termed a silyl cation. By the same reasoning, the presence of three normal covalent bonds and one very weak fourth interaction indicates that the structure has more tricoordinate than tetracoordinate character. By contrast, the C-C distance in the σ complex of CH_3 to an arene cited by us (1) is 1.56 Å (5). This number is very close to the normal value of 1.54 Å in propane or adamantane (1) and corresponds to a bond order n of 0.93 and to essentially tetracoordination. We thank Pauling for providing this refinement, which enables us to specify more quantitatively the nature of the interaction between Si and toluene in our structure.

The comment by Olah *et al.* contains (i) a product study, (ii) theoretical calculations of geometry, (iii) theoretical calculations of chemical shifts, and (iv) comments on another recently published report by Reed *et al.* (6). We shall comment about the first three subjects in turn and shall defer to Reed *et al.* on the fourth.

The observation of (triethylsilyl)toluene is not relevant to an assessment of the extent of bonding between Si and toluene in the stable ion observed by us in solution and in the solid, as the same product would be expected both from the σ complex (arenium ion) that Olah *et al.* find in the gas phase by their calculations and from the distantly coordinated system that we observed in the solid. "Inconceivable" notwithstanding, there is firm evidence that these arenes do not react with trialkylsilylium in solution. Reed *et al.* (6) recrystallize their compounds from toluene without reaction. Both Olah and Reed maintain that the carborane anion is less nucleophilic than our borate. It does not follow then that the supposedly more closely bound (to anion) Si ion in our case is more likely to react with toluene. We have observed that toluene and other solvents exchange rapidly on the NMR time scale between bound and unbound states with the silyl cation (7). Thus triethylsilylium exhibits only one ^{29}Si peak in a mixture of benzene and toluene, with a chemical shift intermediate between those in the pure solvents. A "reaction" as envisaged by Olah *et al.* would have led to two distinct σ complexes. In the system methyldiisopropylsilylium tetrakis(pentafluorophenyl)borate, the isopropyl methyls are homotopic in the ^1H and ^{13}C spectra, again indicative of fast exchange. If the exchange of solvent on Si is dissociative rather than associative, as argued by both Boudjouk (8) and Tilley (9), an upper limit of about 15 kcal mol^{-1} may be placed on the barrier to dissociation of Si from toluene, for the given temperature and chemical shift difference. Such an observation does not support a "reaction," but again is more akin to the energetics of H bonds or electrostatic interactions.

With regard to theoretical calculations of geometry, there are appreciable and systematic differences between the gas phase geometry calculated by Olah *et al.* and the observed geometry in the solid. The calculations by Schleyer *et al.* (10) were at a higher level (MP2(fc)/6-31G* for the H_3Si^+ structure), but suffered from a similar lack of agreement with the observed structure. (See figure 1 of the comment by Olah *et al.* for the numbering of atoms.) (i) The calculations indicate more pronounced alternation of bond lengths within toluene, 1.424/1.370/1.403 Å according to Olah *et al.* and 1.429/1.367/1.405 Å according to Schleyer *et al.*, as opposed to 1.40/1.37/1.38 Å observed by us (*1*). (ii) The geometry around C4 is calculated to be rather different from that of sp^2, as illustrated by Olah *et al.* The H attached to C4 is depicted as deviating significantly from the aromatic plane. Schleyer *et al.* (*10*) calculated the C3-C4-H angle to be 117°, whereas we observed it to be 120.5°. Neither group reports the extent of deviations of C4 from the plane of the remaining five atoms, but we expect that calculated deviations are significant, as in figure 1 of the comment by Olah *et al.* The observed toluene molecule, however is essentially planar, the largest C-C-C-C dihedral angle being 1.7°. (iii) The calculations misplace the Si atom considerably with respect to the arene ring, as best illustrated by the Si-C4-C1 angle, calculated by Olah *et al.* to be 110.3°, calculated by Schleyer *et al.* to be 114°, and measured by us in the crystal to be 104°. In general, the calculations give a much tighter binding between Si and toluene, as might be expected for an ion-molecule complex in the gas phase. Thus the theoretical calculations lead to misintepretation of the observed structure in the crystal.

The theoretical calculations of Olah *et al.* and Schleyer *et al.* indicate that the ^{29}Si chemical shift reflects geometry more than positive charge density. The observed chemical shift of about δ 80 to 90 reflects the geometry of the trialkylsilyl portion of the structure, which is well reproduced by calculation, but does not address the critical issues of the positive charge density on Si and the bond order between Si and the arene. The experimental values of chemical shift are perfectly reasonable for Si with low bond order to toluene and high positive charge density.

The operational definition of a silylium ion is that positive charge is predominantly on Si, whereas that of an arenium ion (σ complex) is that positive charge is found predominantly on the arene ring and its substituents. The distinction may be made by quantifying the bond order between Si and the para C of toluene and by quantifying the amount of positive charge on Si and toluene. As noted above, Pauling's equation estimates the Si-C bond order to be 0.28 to 0.35. Schleyer *et al.* (*10*) calculate the gas-phase Wiberg bond index to be 0.44 for the complex of benzene with H_3Si^+. The value should be lower for Me_3Si^+ and even lower in the condensed phase, so that modern theory is in fundamental agreement with Pauling's method which shows that there is only about a third of a bond between Si and toluene. Schleyer *et al.* calculate an association energy of about 30 kcal mol^{-1} between Me_3Si^+ and toluene in the gas phase, and a lower value should be observed in condensed phase, as indicated by fast exchange on the NMR time scale. Compared with a full C-Si bond dissociation energy of 90 kcal mol^{-1} (*11*), the calculated energies also suggest about a third of a covalent bond.

The amount of charge on atoms is a more difficult quantity to assess. Schleyer *et al.* (*10*) calculate the charge on Si in the gas-phase complex between Me_3Si^+ and toluene to be +0.71, leaving only a small amount of charge to be distributed over the atoms of toluene. For comparison, they calculate +0.43, in the neutral methylsilane. We have been able to assess the amount of charge in toluene experimentally by examining the ^{13}C shifts in the solid (*7*). Introduction of positive charge into toluene in a σ complex of the type illustrated by Olah *et al.* should result in appreciable downfield movement of the chemical shift for C1/C3/C5, upfield movement for C4, and downfield movement for CH_3. In the solid state, however, all these resonances are essentially unchanged from those of free toluene. Thus experiment does not support the σ complex model. None of our observations, however, are in disagreement with the η_1 π complex model of Reed *et al.* (*6*), which is expected to have an undistorted, planar toluene ring and charge predominantly on Si.

In summary, theoretical calculations of bond order, theoretical calculations of charge density on Si, theoretical and experimental assessments of association energies (when differences between gas and condensed phase are taken into consideration), experimental determination of ^{13}C chemical shifts of bound toluene, and observation of fast exchange on the NMR time scale all indicate that there is about a third of a covalent bond or less between Me_3Si^+ and toluene and that the preponderance of positive charge is on Si. Consequently, as we concluded in our report, triethylsilylium tetrakis(pentafluorophenyl)-borate is best termed a silyl cation with weak coordination to toluene.

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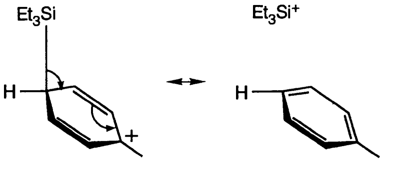
Response: The description of Et_3Si-(toluene)$^+$ as a σ silylated arenium ion by Olah *et al.* [and by Schleyer *et al.* (*1*)] appears to arise from an emphasis on calculated structure in preference to observed structure and from the expectation that Si chemistry will closely follow C chemistry. It is becoming apparent however, that unlike carbenium ion (R_3C^+) chemistry, that for the silylium ion can be approached incrementally. Thus, Et_3Si(toluene)$^+$ is a hybrid of a π-complexed silyl cation and a σ-complexed arenium ion (Scheme 1). The legitimate polemic then becomes one of degree. We concur with Lambert *et al.* that the observed structure is consistent with a predominant contribution from a positively charged Si rather than C species. Theoretical calculations at the HF/6-31G* level produce a value for the critical Si-C-C_{para} angle that is too large by about 6° to 10°, thereby conferring artifactual predominance of the arenium ion structure.

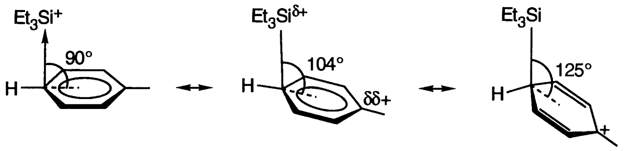
Olah *et al.* and Schleyer *et al.* (*1*) state that Si hyperconjugation could explain the long Si-C distance (2.18 Å). Hyperconjugation contributes a further resonance form of the very type they discount, that is, one with ionic R_3Si^+ and no covalent bond.



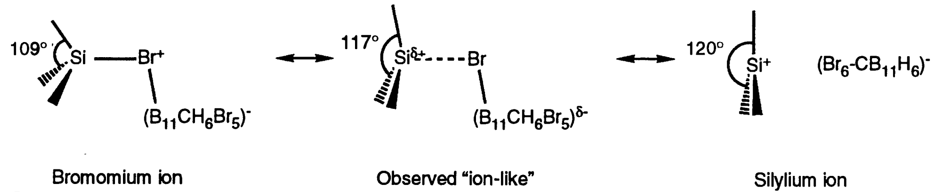
Cationic hyperconjugation

In fact, it was the original description by Lambert *et al.* (*2*) of Et_3Si(toluene)$^+$ as a silylium ion where "covalent bonding is weak or absent" that first stirred controversy. Weak π bonding of toluene to Si seems currently to be the best single description of the structure. Certainly the search for a free R_3Si^+ ion must continue, but so must the search for better theory.

In a conceptually related manner, the



Scheme 1



Scheme 2

observed structure of $i\text{-Pr}_3\text{Si}(\text{Br}_6\text{-CB}_{11}\text{H}_6)$ can be viewed as lying on a continuum between a bromonium ion and a silylium ion (Scheme 2). In describing $i\text{-Pr}_3\text{Si}(\text{Br}_6\text{-CB}_{11}\text{H}_6)$ as a "silylbromonium zwitterion," Olah *et al.* underestimate the contribution of silylium ion character. One can argue about degree, but by the criterion of the C-Si-C angle (117° is observed), the major contributor has silylium rather that bromonium ion character. The silylium ion character is also strongly reflected in the chemical reactivity of $i\text{-Pr}_3\text{Si}(\text{Br}_6\text{-CB}_{11}\text{H}_6)$. It rapidly abstracts chloride from dichlorobenzene and strongly bound fluoride from fluorobenzene.

In summary, while the metaphor "you can't get half pregnant" may apply to carbenium ion chemistry, in silylium ion chemistry the important thing is "being more than halfway through pregnancy." The various criteria currently available for measuring closeness to full-term R_3Si^+ character (^{29}Si NMR, theory, C-Si-C bond angles, reactivity, and so on) give different estimates. But the establishment of substantial, and by most criteria predominant, silylium character in both $i\text{-Pr}_3\text{Si}(\text{Br}_6\text{-CB}_{11}\text{H}_6)$ and $\text{Et}_3\text{Si(toluene)}^+$ cannot be denied.

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Ca^{2+}-Induced Ca^{2+} Release in Response to Flash Photolysis

S. Györke and M. Fill (*1*) recently used results obtained with DM-nitrophen (caged Ca^{2+}) photolysis to support the hypothesis that Ca release channels from cardiac muscle may "adapt" to a Ca^{2+} stimulus. According to this proposal, a relatively rapid rise in the concentration of Ca^{2+} ([Ca^{2+}]) (from about 0.1 μM to 0.2 μM) on the cytoplasmic side of the Ca channels results in the probability that Ca channels of the cell will open (P_O) to increase to a high value and then gradually decline to a lower, steady value (Fig. 1A). Their conclusion was based on the assumption that [Ca^{2+}] rises in a step-like fashion after the photolysis of the DM-nitrophen, and this assumption was apparently supported by measurements with a Ca^{2+}-sensitive electrode. However, the photolysis procedure used by Györke and Fill would have generated an extremely large, transient increase in the [Ca^{2+}] (*2, 3*) (Fig. 1B), which itself might account for the behavior of the channels without there having to be any Ca channel "adaptation."

The occurrence of a Ca^{2+} "spike" in response to photolysis of DM-nitrophen can be explained as follows. Györke and Fill added 3 mM total nitrophen and 2 mM $CaCl_2$ (*1*), so initially there would have been 2 mM of Ca-nitrophen and 1 mM of free nitrophen in the solution, and thus 0.5 mM of the total nitrophen must have been photolysed in order to raise the steady-state [Ca^{2+}] by a factor of 2. As the quantum efficiency of Ca-nitrophen is 2.5 times that of free nitrophen (*3*), the laser flash would have liberated about 0.42 mM of Ca^{2+} from Ca-nitrophen. Because this liberation would have been faster (half-time <180 μs) (*4*) than the association of Ca^{2+} with the remaining free nitrophen (initial half-time about 1 ms) (*3*), the free [Ca^{2+}] would have increased briefly to about three orders of magnitude greater than the final steady-state concentration (Fig. 1). In order to raise the steady state [Ca^{2+}] by a factor of another 2.5, the second laser flash must have photolysed about 0.27 mM Ca-nitrophen and hence generated another large, though slightly smaller, Ca^{2+} spike. (Even if the free nitrophen were only 0.1 mM, owing to a possible error in the calculated total amount of added nitrophen, the Ca^{2+} spikes would still be two orders of magnitude greater than the change in steady [Ca^{2+}].) Such Ca^{2+} spikes would not have been detected by the Ca^{2+}-sensitive electrode used by Györke and Fill, which only responded with a time constant of 30 to 50 ms (dotted line in Fig. 1B). Nevertheless, the Ca release channels should have responded acutely to such a fast transient [Ca^{2+}] change (the half-activation time was stated as 1.2 ms) (*1*), with the probability of being open rising markedly during the Ca^{2+} spike before settling to a lower value after the [Ca^{2+}] reached steady-state.

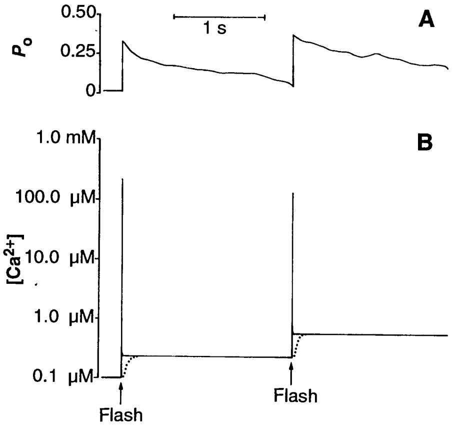

Fig. 1. Channel activity in response to changes in [Ca^{2+}] [modeled on data in figure 3 of (*1*)]. (**A**) Change in the probability (P_o) of a cardiac Ca^{2+} release channel being open. (**B**) Time course of [Ca^{2+}] resulting from flash photolysis of DM-nitrophen, calculated (solid line) and as measured by a Ca^{2+}-sensitive electrode (dotted line).

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